The origin and evolution of the porosity within the dolomitised carboniferous limestone of the Wirksworth area, Derbyshire

Thesis

THE ORIGIN AND EVOLUTION OF THE POROSITY WITHIN THE DOLOMITISED CARBONIFEROUS LIMESTONE OF THE WIRKSWORTH AREA, DERBYSHIRE.

A thesis presented for the degree of

Doctor of Philosophy

by

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January 1981

Date of submission: 1-1-81

Date of award: 6-8-81

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ABSTRACT

A detailed study of the porosity development in the dolomitised Lower Carboniferous Limestone of the Wirksworth area has revealed a complex diagenetic history. The massively-bedded Asbian and Brigantian micarenites and sparenites became indurated largely during the Lower Carboniferous, within the active phreatic zone (saturated groundwater zone). The very high porosities of the carbonate sediments became occluded during this phase of diagenesis, to give the characteristic limestone porosity (2 - 8 percent).

Dolomitisation occured prior to the late Triassic mineralisation, either at depth beneath the cover of Middle and Upper Carboniferous sediments or during the exposure of the limestone through the Edale Shales (Namurian) beneath the Zechstein Sea (Permian). Jointing has been shown to have had a primary control upon dolomitisation, although karstification, developed during the pre-Namurian exposure of the limestone, and stylolitisation were also important processes.

The dolostones consist mainly of xenotopic-hypidiotopic types showing many calcite-filled polyhedral pores, although less common xenotopic and idiotopic dolostones do occur. The completely dolomitised xenotopic dolostones are thought to represent dolomitised micarenites, whilst the less completely dolomitised hypidiotopic and idiotopic

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CHAPTER ONE

1. INTRODUCTION

For many centuries the importance of carbonates as suitable reservoirs for natural resources has been recognised. However, during the 20th Century our understanding of the development of porosity in carbonate rocks has come from our unparalled dependence upon petroleum. More than 45 percent of the world's petroleum reserves are reservoired in carbonates. In the Middle East, where more than half of the world's reserves are located, most of the oil production comes from carbonate reservoirs and considerable quantities of oil are produced from carbonate rocks in the U.S.A. and the U.S.S.R. Thus the study of carbonate reservoir rocks is of more than academic interest.

The origin and classification of carbonate porosity has been described by Howard (1928), Howard and David (1936), Imbt and Ellison (1946), Hohlt (1948), Archie (1952), Chilingar and Terry (1954), Waldschmidt et al.,(1956), Chilingar (1956), Murray (1960), Weyl (1960), Harbaugh (1967), Choquette and Pray (1970) and Aoyagi (1973), these authors have highlighted the very complex nature of the development of the porosity, due to the many depositional and post-depositional processes involved. A central theme to most of the classifications is the two-fold division into primary (depositional) and secondary (post-depositional) porosity. The most comprehensive and widely accepted study of

nomenclature and classification of carbonate porosity is that of Choquette and Pray (1970). They have further divided primary porosity into predepositional and depositional, and secondary porosity into three stages, the early burial or "eogenetic" stage, the late near-surface or "telogenetic" stage and the normally very long intermediate or "mesogenetic" stage, occurring at depths below any major influence of surface processes. They recognise fifteen basic porosity types based upon fabric selectivity, that is those that are fabric selective which includes interparticle, intraparticle, intercrystal, mouldic, fenestral, shelter and growth framework porosities, and those that are "non-fabric selective" which include fracture, channel, vug and cavern porosities. Four types of porosity not conforming to this two-fold classification are termed "fabric selective or not" and include breccia, boring, burrow and shrinkage porosities. The classification works equally well for dolostones wherein most of the porosity types can be identified. However, many of these porosities may have been inherited from pre-existing limestones.

Choquette and Pray together with Howard (1928), Howard and David (1936), Imbt and Ellison (1946), Hohlt (1948), Murray (1960) and Harbaugh (1967) and Steiglitz (1975), place great emphasis upon subaerial dissolution, as a major source of carbonate porosity. This is developed principally, but not exclusively, during a later near-surface stage of diagenesis (telogenetic). The process can

modify pores to form enlarged vugs or more extensively form larger features such as channels and caverns. These are all features of karstification.

Karstified carbonate formations are recognised as being a major source of petroleum, metallic and non-metallic minerals and water. Howard (1928) stated that 95 percent of known carbonate petroleum reservoirs were karstified and many have been recorded since from rocks as old as Precambrian to Tertiary. Using the Choquette and Pray (1970) classification, a simple division of carbonate petroleum reservoirs can be made which is very similar to that given by Howard (1928). The fabric selective porosities which are mainly primary can be found to form stratigraphic traps (Levorsen 1954) see Table I. The non-fabric selective porosities can have a profound effect upon reservoir characteristics. Fractures occur probably in all reservoirs, but do not constitute the major source of porosity. There are fields however where the primary carbonate porosity is low and the effective porosity is due to fracturing (see Table I). Fractures also play a very important part in the development of karstification which enhances the porosities and permeabilities of many reservoirs. These are the palaeogeomorphic traps of Martin (1966) (see Table I).

Dolomite forms the reservoir rocks of so many fields that it deserves special mention. Its porosity is mainly

POROSITY TYPES AND EXAMPLES	LOCATION	AGE of RESERVOIR	PUBLICATION
Intraparticle and growth framework porosities			
Golden Spike Field	Alberta, Canada.	Devonian	Walls (1976)
Beaver Hills Field	Alberta, Canada.	Devonian	Hemphill & Smith and Szabo (1970)
Boyd - Peter Reef	Michigan, U.S.A.	Silurian	Ferris (1972)
Ekofisk Field	North Sea. U.K.	Cretaceous	Scholle (1977)
Interparticle porosity			
Chester Field	Oklahoma, U.S.A.	Carboniferous	Lucia and Murray (1967)
Paradox Basin Fields	Col. - Utah - N. Mex - Ariz.	Carboniferous	Norman and Rawson (1976)
Swan Hills Field	Alberta, Canada	Devonian	Edie (1961)
Chailly Field	France.	Jurassic	Cussey and Friedman (1977).
Ghawar Field	Middle East.	Jurassic	Steinke et al (1958)
Damman Field	Middle East.	Jurassic	Thralls and Hesson (1957)
Minagish, Umm Gudar and Burgan Fields.	Kuwait	Cretaceous	Illing et al (1967)
Fracture porosity			
San Juan Basin	New Mexico. U.S.A.	Cretaceous	Gorham et al (1979)
Hortense Field	Texas, U.S.A.	Cretaceous	Doyle (1955)
Lacq Field	France.	Cretaceous	Winnock and Pontalier (1970)
Reitbrook Field	Germany.	Cretaceous	Tiratsoo (1971)
Schonkirchin - Tief Field	Austria	Triassic	Hawle et al., (1967),
Baumgarten - Zwerndorf Field	Austria	Triassic	Hawle et al., (1967),
Ayoluengo Field	Spain	Jurassic	Sanz (1967),
Retchitsky and Ostashkovitchsky Field (Prepiatsky Basin)	U.S.S.R.	Devonian	Avvakumov et al., (1967)
Enhanced intraparticle and growth framework porosities			
Sirte Basin.	Libya.	Tertiary	Terry and Williams (1959)
Chevosakiva - Garodki Field	U.S.S.R.	Permian	Tiratsoo (1971)
Enhanced intercrystalline porosity			
Zelten Field	Libya.	Tertiary	Bebout and Pendexter (1975)

Table I Oil and gas fields of the world, showing various types of porosity. The classification used is that of Choquette and Pray (1970)

POROSITY TYPES AND EXAMPLES	LOCATION	AGE of RESERVOIR	PUBLICATION
Enhanced interparticle porosity			
Andrews South Field	Texas U.S.A.	Devonian	Lucia and Murray (1967)
Golden Lane Fields	New Mexico, U.S.A.	Cretaceous	Viniegra and Castillo-Tejero (1970)
El Abra Field	New Mexico, U.S.A.	Ordovician	Aguayo (1976)
Volga - Urals Field	U.S.S.R.	Carboniferous	Sarkisyan et al (1973)
Dolostone porosity			
Panhandle - Hugoton Field	Kansas, Oklahoma and Texas, U.S.A.	Permian	Pippin (1970)
Yates Field	Texas, U.S.A.	Ordovician	Howard (1924)
Big Lake Field	Texas, U.S.A.	Permian	Hennen (1929)
Deep River Field	Michigan U.S.A.	Devonian	Landes (1948)
Leduc Field	Alberta, Canada.	Devonian	Layer et al (1949)
El Rassak, Yidma and Alamein Fields	Middle East.	Cretaceous	Metwalli and El Hady (1975)
Lacq Field	France	Cretaceous	Winnock and Pendexter (1970)
Enhanced dolostone porosity			
Apco Field	Texas, U.S.A.	Permian	Ellison (1948)
Dollarhide Field	Texas, U.S.A.	Ordovician – Silurian	Stormont (1949)
Edward Field	Texas, U.S.A.	Cretaceous	Cook (1979)
Spindletop Field	Texas, U.S.A.	—	Barton and Parson (1925)
Healdton Field	Oklahoma, U.S.A.	Ordovician	Latham (1970)
Oklahoma City Field	Oklahoma, U.S.A.	Ordovician	Webb (1976)
Star-Lacey Field	Oklahoma, U.S.A.	Carboniferous	Withrow (1972)
West Campbell Gas Field	Oklahoma, U.S.A.	Silurian – Devonian	Harvey (1972)
Lima - Indiana Field	Kansas, U.S.A.	Ordovician	Rooney (1966)
Bindley Field	Kansas, U.S.A.	Carboniferous	Ebanks et al (1977)
Kraft - Prusa Field	Kansas, U.S.A.	Cambro-Ordovician	Walters and Price (1948)
New Hope Field	Mississippi, U.S.A.	Ordovician	Mellen (1974)
Greenberg Field	Kentucky, U.S.A.	Silurian	Schwalb and Wilson (1972)
Leduc Field	Alberta, Canada.	Devonian	Layer et al (1949)
Rainbow Area Fields	Alberta, Canada.	Devonian	Andrichuk (1958)
Ragusa and Gela Fields	Sicily.	Triassic	Vercellino and Rigo (1970)
Haupt dolomit	Austria.	Triassic	Tiratsoo (1971)

Table II Oil and gas fields of the world showing various types of porosity. The classification used is that of Choquette and Pray (1970)

intercrystalline, but can inherit mouldic, interparticle, growth-framework and interparticle porosities from the former limestones (see Table II). Many fields have also been formed due to the leaching of dolomite to give enhanced porosities (see Table II).

The importance of karst as a locus in which certain mineral deposits can accumulate has been documented by many authors. Good reviews of karst and economic deposits are given by Bernard (1973) and Zuffardi (1976). Although almost all types of minerals have been discovered associated with karst (see Quinlan, 1972 and Zuffardi, 1976), it is the variously termed Lead-Zinc Limestone Association (Stanton, 1972), Mississippi Valley Type or Alpine Type, which have received most comment. These constitute some of the world's greatest sources of lead and zinc and are the principal sources of these metals in the United States and Europe and yield large quantities of lead and zinc in Canada and North Africa.

It is the greatly enhanced porosities and permeabilities that are the major controlling factors upon the localisation of the deposit, Jackson and Beales (1967) and Snyder (1967) however, believe that a further factor that influences the localisation of these deposits is the presence of sulphates in the carbonates which under the influence of sulphate reducing bacteria produce the necessary sulphide ions to

LEAD-ZINC SULPHIDE BODIES	LOCATION	AGE of DEPOSIT	PUBLICATION
Dolostone related deposits			
Austinville - Ivanhoe district,	Virginia, U.S.A.	Cambrian	Brown and Weinberg (1968)
Friedensville Mine,	Pennsylvania, U.S.A.	Cambro-Ordovician	Callahan (1968)
Mascot Jefferson City District	Tennessee, U.S.A.	Ordovician	Crawford and Hoagland (1968)
Eureka Area,	Nevada, U.S.A.	Cambrian	Nolan and Hunt (1968)
Gilman District,	Colorado, U.S.A.	Carboniferous	Radabaugh et al (1968)
Leadville District,	Colorado, U.S.A.	Cambrian-Carboniferous	Tweto (1968)
East Tennessee Deposits	Tennessee, U.S.A.	Ordovician	Carpenter et al (1971)
Southern Appalachian Deposits,	U.S.A.	Ordovician	Maher (1971)
The Newfoundland Deposits,	Canada.	Ordovician	Collins & Smith (1975)
Thunder Bay District,	Ontario, Canada.	Pre-Cambrian	Franklin and Mitchell (1977)
Cornwallis District,	Canadian Arctic	Devonian	Kerr (1977)
Robb Lake District,	British Columbia, Canada	Devonian	Macqueen and Thompson (1978)
German deposits	—	Permo-Triassic	Taupitz (1967)
Sardana region,	Siberia.	Pre-Cambrian	Ruchkin et al (1979)
Zeerust Area,	Transvaal, S. Africa.	Pre-Cambrian	Martini (1975)
Bulman Area,	Northern Territory, Australia.	Pre-Cambrian	Patterson (1965)
Limestone - dolostone boundary related deposits			
Mid-Continental Deposits,	U.S.A.	Carboniferous	Snyder (1968)
Southern Pennines,	U.K.	Carboniferous	Ford (1969)
Limestone related deposits			
Illinois and Kentucky deposits.	U.S.A.	Devonian-Carboniferous	Grogan and Bradbury (1968)
S.E. Missouri Deposits,	U.S.A.	Cambrian	Snyder and Gerdemann (1968)
English Pennines,	U.K.	Carboniferous	Dunham (1952)
Salfossa Deposit,	Italy.	Triassic	Lagny (1969)

Table III Lead-zinc sulphide bodies of the world, which are associated with carbonate rocks.

combine with the metallic chlorides of connate waters to give the metallic sulphides. This may explain the great affinity these deposits have for dolostones, due to the common association of dolostones and evaporites.

There is much debate about the origins of these lead-zinc deposits. Many believe that the deposits have a magmatic origin (Callahan 1967, Campbell 1967,Brown and Weinberg 1968) while others compromise and see a mixing of connate brines and magmatic fluids as being the origin (Heyl 1967, Grogan and Bradbury 1968, Dunham 1967, Roedder 1967, White 1968). A more detailed review of the various origins of these deposits is given by Brown (1970).

The Pine Point deposit, possibly the largest lead-zinc deposit in the world, is a good example of this type. Here the "reef buildups " of the Presqu'ile Formation became dolomitised and later subjected to subaerial erosion to give the characteristic cavernous and vuggy porosities. The deposits are plumb-shaped and are mainly associated with dissolution collapse-breccia, so common with this type of deposit. Dolostone is the dominant rock type as indicated by Table III.

Lead-zinc is also commonly associated with limestone formations and limestone-dolostone lateral and vertical. boundaries, which were cavernised prior to mineralisation.

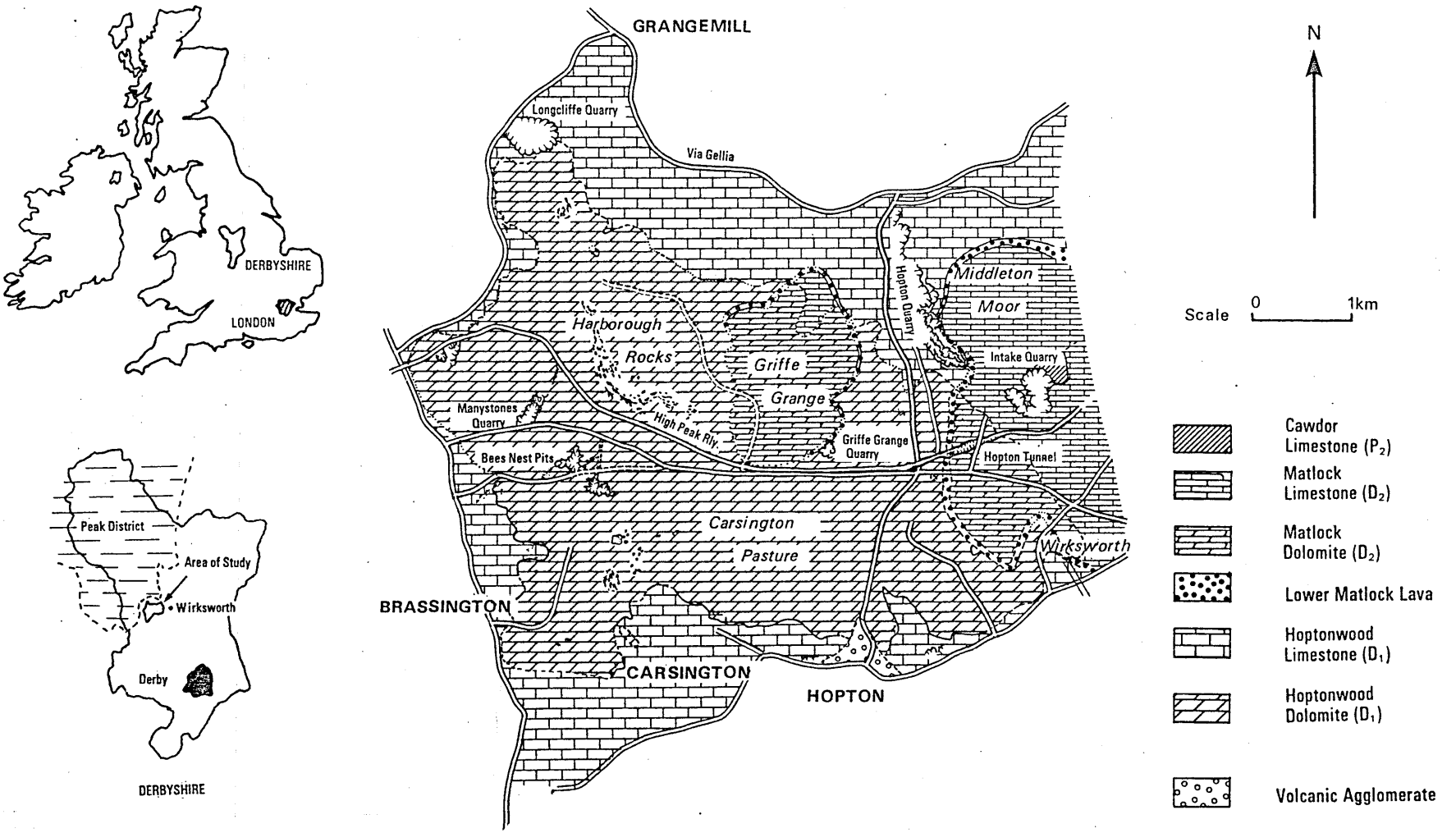

Figure 1. Location map of the study area indicating, stratigraphy, area of dolomitisation and the position of significant quarry sections.

Carbonate aquifers are important contributors to our total water resources e.g. the Chalk of the London and Paris Basins. Karstification both modern and ancient has greatly influenced reservoir porosity and permeability. Palaeokarst can be found to give high yields and to strongly influence the present-day circulation of reservoirs e.g. the Damman Limestone, Kuwait (Burdon and Al-Sharhan, 1968).

1.1. Aims of this Study

In the foregoing paragraphs it is abundantly clear that dolomitisation and karstification are important factors in developing potential reservoirs and repositories for natural resources. For this reason alone this investigation was undertaken to study the development of porosity within a dolostone formation at the present-day weathering surface. It can be shown that the majority of porosity profiles, constructed from the many boreholes drilled in the area, show no real pattern. Thus a prediction of the distribution of porosity within a formation is impossible. Our aims were to try to understand the development of this secondary dolostone porosity which is due mainly to karstification. It was felt that a common feature of these dolostones, namely dedolomitisation, had a profound effect upon the development of porosity and this was studied in some detail. The project involved the study of a 25 sq. km. area of dolomitised Carboniferous Limestone in the Southern Pennines between Wirksworth and Brassington in Derbyshire. (see figure 1). The area was chosen because of the numerous quarry and railway cutting sections.

C H A P T E R T W O

2.1. The Stratigraphy of the Carboniferous Limestone Succession in the Wirksworth Area, Derbyshire

The Lower Carboniferous Limestone succession of the Derbyshire Dome, consists largely of massively bedded limstones. The shelf sequence, largely Asbian and Brigantian in age (approximately D1, D2 and P2 subzones), contains several important beds of basalt, tuff and clay (Walkden 1972). The earliest geological study was included in Whitehurst's book (1778) later developed by Pilkington (1789) and Watson (1811). One of the first geological maps was produced by Fairey (1811) and 1869 saw the publication of the first memoir by Green et al., with its second edition in 1887. The Wirksworth area was studied in greater detail during the twentieth century; Sibly (1908) studied the faunal succession, Gibson and Wedd (1913) included a comprehensive account of the area in their memoir, Shirley (1959) studied the unconformable nature of the different limestone Groups, Eden et al., (1958) divided the succession stratigraphically into local groups and Smith et al., (1967) compiled the most recent memoir.

In the study area the limestone formation consists largely of the Hoptonwood and Matlock"Groups", separated by the Lower Matlock Lava (fig.1). The youngest limestones

in the area lie within the 'Cawdor Group', but these are poorly developed in the area and are only seen at Intake Quarry (ref. 271551) (pl. 1) and Baileycroft Quarry (ref. 286544) and as far as can be seen have not been subjected to dolomitisation in the area studied. The succession is as follows:-

STAGE	ROCK UNIT	THICKNESS
	Cawdor Group(P_2)	c. 10metres exposed
Brigantian	Matlock Group (D_2)	up to 80metres
	Lower Matlock Lava	up to 7metres
Asbian	Hoptonwood Group (D_1)	up to 80metres

Following the stratigraphic code published by the American Commission on Stratigraphic Nomenclature (1961), it is felt that these limestones should more rightfully be divided into formations, rather than groups. As their nature corresponds more closely to the definition of a formation given by The Commission; "The formation is the fundamental unit of rock stratigraphic classification. A formation is a body of rock characterised by lithologic homogeneity; it is prevailingly but not necessarily tabular and is mappable at the earth's surface or traceable in the sub-surface". In contrast to a group which is defined as being composed of two or more formations. All the groups of this study have a great deal of lithologic homogeneity, the only obvious lithological variation being the clay wayboards thus they are thought to comprise formations. However as this study is primarily concerned with the porosity development in the stratigraphically

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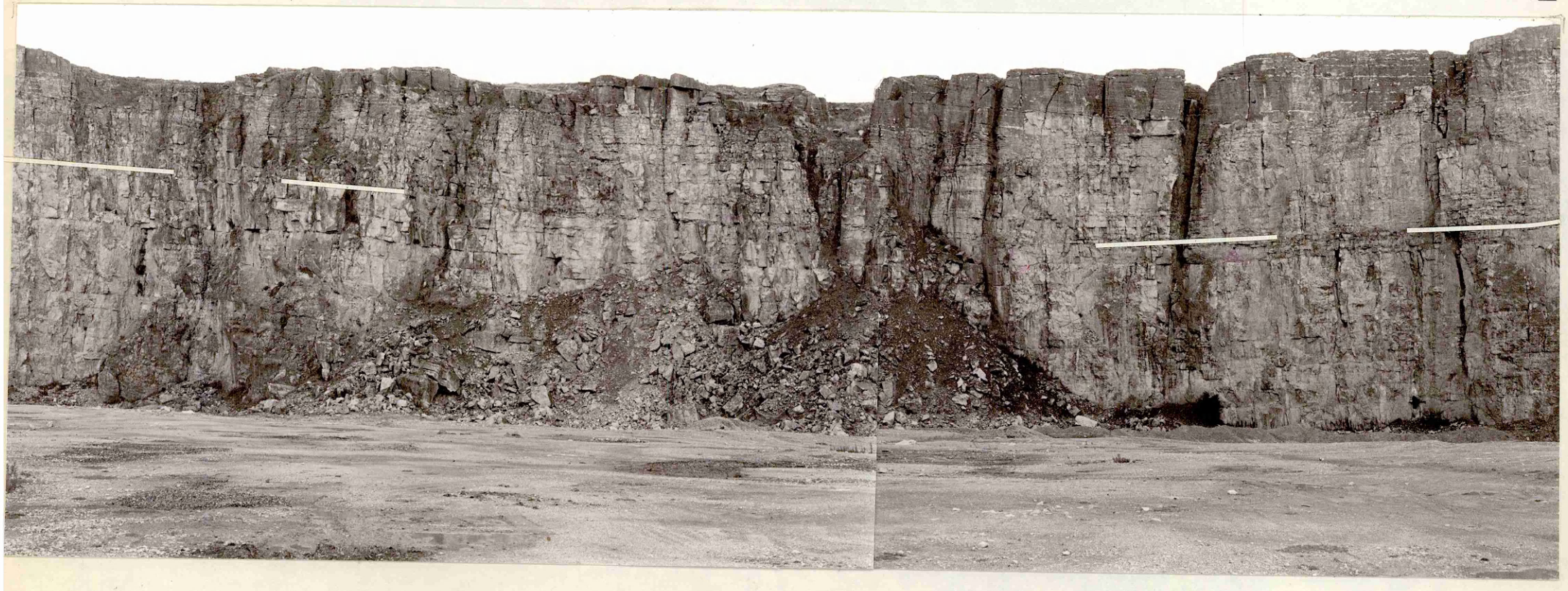

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equivalent dolostones, it is felt beyond the scope of this study to discuss this matter in detail. Thus, although being fully aware of this misnomer, the term "Group" is retained to prevent any confusion.

Shirley demonstrated that the "Groups" can be shown to have unconformable relationships. The upper unconformity between the Cawdor and Matlock "Groups" can be seen in the Wirksworth area, at Baileycroft and Stoneycroft Quarries where the Cawdor "Group" overlaps the Matlock "Group" to lie directly upon the Hoptonwood "Group". The unconformity can also be seen cutting across the Matlock "Group" at Intake Quarry (pl. 1). The Lower Matlock Lava is marked in the area by a weathered lava or tuffaceous beds with no angular discordance above or below. The unconformity above the lava has been noted to the north by Shirley and Horsefield (1939) and has recently been studied by Walkden (1977) at Miller's Dale. The succession of limestones is not only broken by lavas and tuffs, but also by numerous clay horizons, locally termed "wayboards". These are thought to represent disconformities, the clays being deposited under subaerial conditions and the commonly associated irregular bases to be a consequence of minor palaeokarstification (Walkden 1970, 1972). These are discussed in greater detail in Chapter VI.

The limestone succession and lithologies were studied principally in three large quarries in close proximity

to the dolostone outcrop. These are Middle Peak Quarry (ref. 282546), Hoptonwood Quarry (ref, 263555) and Intake Quarry, the details of which are given in Appendix I.

2.1. The Hoptonwood "Group"

The Hoptonwood "Group" defined by Eden et al., (1958) in it's type section the Hoptonwood Quarries and the upper part of which is also noted at Middle Peak Quarry, essentially consists of approximately 80 m. of massively bedded pale grey fossiliferous limestone. Macrofossils are rare, but brachiopods and other shell fragments, corals and crinoid stems do occur. The majority of the fossil material has been fragmented to calcarenite. The predominant fossil material is crinoidal, mainly ossicles, which are corroded, micritised and often show well-developed syntaxial rims, both cement and neomorphic. Brachiopod fragments are also abundant, mainly productids, showing the pseudo-punctate structure of their shells. The detail of their structure has been retained through diagenesis as with most of the other fossil material present, such as algae, bryozoa, foraminifera, gastropods, ostracods and corals. Reefs are common in the lower Asbian, particularly at Castleton and towards the west (Shirley and Horsefield, 1939). In the Wirksworth area reef limestones have been noted near Godfreyhole (ref. 271537) just south of the dolostone outcrop (Shirley, 1959).

The major lithologies are biomicarenites and biomicrosparenites.* Any lateral and vertical variation is due to the varying amounts of fossil material present. Biosparenite and oosparenite are commonly, although not exclusively, associated with clay wayboards, as noted by Walkden (1977) at Miller's Dale. The oolite consists mainly of rounded shell fragments with isopachous oolitic coatings (pl. 4a). The sparenites also occur at the top of Hoptonwood Quarry, immediately below the Lower Matlock Lava (Appendix I). A similar occurence has been noted at Middle Peak Quarry, except that the lava is absent and marked by tuffaceous shaley bands (Appendix I). However, there are two shaley horizons separated by the biosparenites and oosparenites (fig. 2). Lithologically the junction between typical Hoptonwood and Matlock "Groups" occurs at the upper shaley band. The fossil evidence is sparse, but the lower shaley band does have associated with it, abundant gigantoproductids which only rarely occur in the Hoptonwood group, and are a hallmark of the Matlock Group. The exact positioning of the junction is felt to be beyond the scope of the study.

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* The classification used during this study is that of Folk (1959). It was felt that the classification suits this study due to its petrographic nature. It will be shown in Chapter IV that the petrography of these limestones has great influence upon the type of dolostone developed.

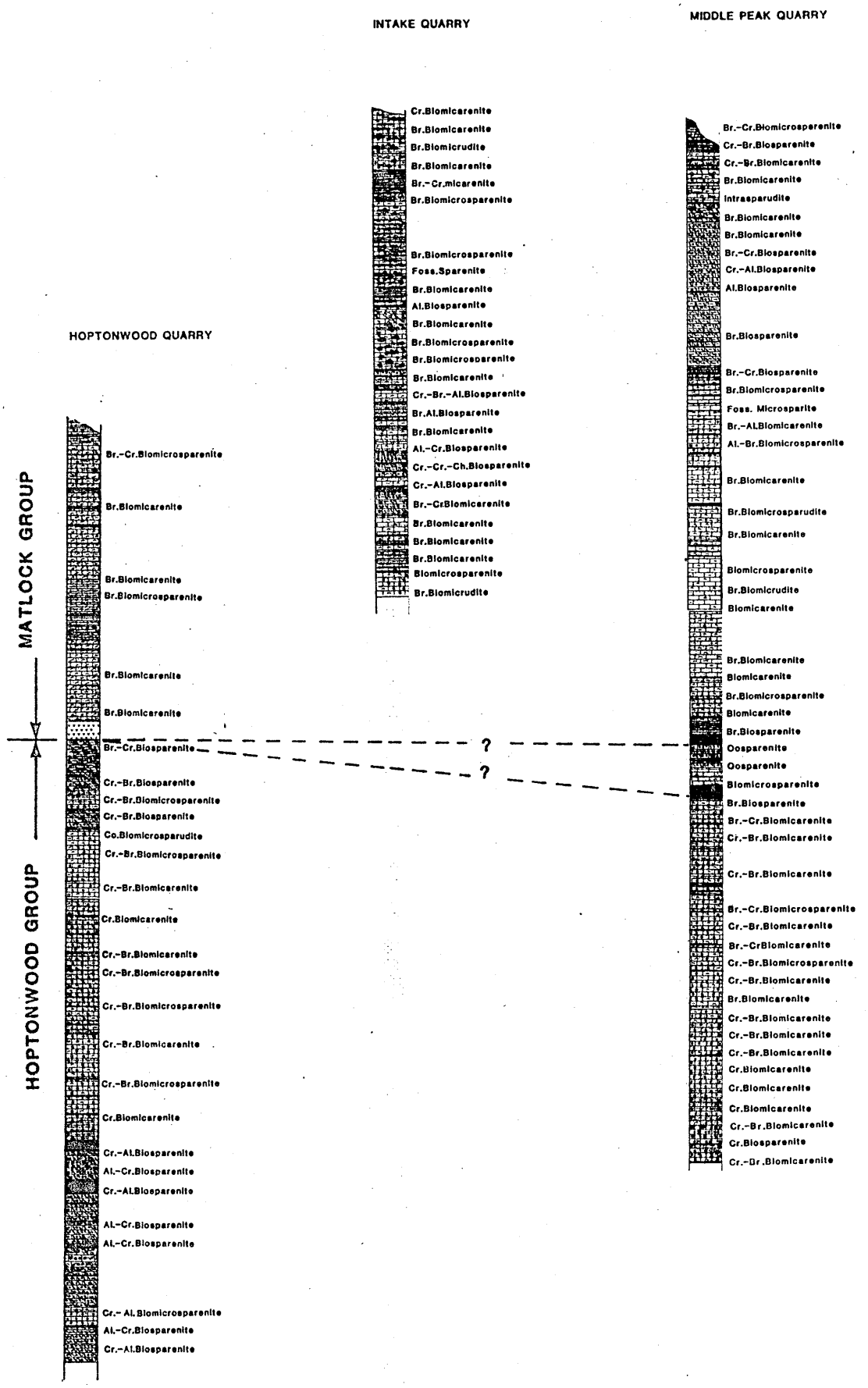


Figure 2 A correlation of the different quarry sections studied. indicating the position of the junction between the Hoptonwood and Matlock Groups and the uncertainty of that junction in Middle Peak Quarry.

The succession is interrupted by numerous small clay wayboards which have been noted at Hoptonwood and Middle Peak Quarries (Appendix 1). These consist of yellow-brown clay, usually only a few tens of centimetres thick, although sometimes as much as 50cms thick. Some exhibit an irregular base, possibly equivalent to the karstic features noted by Walkden.

2.2.The Lower Matlock Lava

The main features of the outcrop of the Lower Matlock Lava have been described in detail by earlier workers (Arnold-Bembrose 1894 and Gibson and Wedd 1913) in the Matlock area. This unit within the study area is marked by a blue-green to yellow-brown clay, depending upon the extent of weathering. This is seen at Hopton Tunnel, (ref.264547) and Griffe Grange Quarry (ref. 255548). At Middle Peak Quarry it appears as a tuffaceous shaley band. The only locality where an identifiable igneous rock can be collected is towards the top of Hoptonwood Quarry (Appendix 1). This is badly weathered and very little of the original textures remain, although it's basaltic nature can be identified. To the north of the area, at Bonsall Wood Basalt Quarry (ref. 283574), Smith et al., (1967) have found the lava to be an olivine basalt, usually amygdaloidal.

2.3. The Matlock "Group"

The Group defined by Eden et al., (1958) in the

Matlock area, consists of 80m of dark massive, though variably bedded biomicarenites and biosparenites. The limestones were studied in detail at Intake and Middle Peak Quarries (Appendix I). The lithologies are similar to those found in the Hoptonwood "Group" except for their colour and dominance of brachiopod fragments. The darker colouration is due mainly to the presence of hydrocarbons and to a lesser extent their clay content. Macrofossils are more abundant than in the Hoptonwood Group, and are mainly gigantoproductids, and are one of the major features used to identify the Matlock "Group" particularly once it has become dolomitised. These brachiopods can be found to form isolated shelly bands. Again, the majority of the fossil material is fragmentary and calcarenitic. The brachiopod fragments comprise typical fibrous productid shells, retaining much of their original fine structure. Other shell fragments appear to have been leached and infilled by a coarser sparry calcite. Crinoidal fragments are also present, although to a lesser extent than in the Hoptonwood "Group", and again are micritised and have well-developed syntaxial rims. Corals, algal fragments, ostracods and foraminifera can also be found.

A great variation in the lithology occurs mainly

vertically with the introduction of biosparenites, although laterally it is the relative amounts of matrix and fossil material that varies (Appendix I). The succession is again broken by a number of clay wayboards. Many have irregular bases and again are believed to be due to karstification. However, many of the limestone beds are irregularly bedded due to pressure dissolution, and thus a similar origin must be considered for the irregular bases of the clays. Unlike the Hoptonwood "Group", cherts are common in the Matlock "Group",occurring mainly along the bedding but do occur in thin beds, particularly at Intake Quarry (pl. 8a). Silicification occurs within the fabric of the rock where brachiopods have been preferentially replaced (sect. 3.2.9).

2.4. The Cawdor Group

The Cawdor "Group" was defined in the area by Eden et al. (1958), after Gibson and Wedd (1913) originally identified the "Group" to the north of the area in Cawdor Quarry. The "Group" was studied in detail at Intake Quarry, and found to consist essentially of bedded biomicarenites with a very good development of bedded cherts. At Intake Quarry the limestones lie unconformably upon the Matlock "Group" and just to the south-west at Baileycroft Quarry overlap to rest on the Hoptonwood "Group".

2.5 Volcanic Agglomerate

The other igneous rock present in the area, is an agglomerate bed occuring near Hopton village (ref. 258534), (fig. 1). The age and origin is unknown. It is one of

several similar bodies occurring in Derbyshire, such as those at Grangemill, near Buxton and Bonsall Moor which are believed to be vent agglomerates (Smith et al., 1967).

CHAPTER THREE

A Petrographic and Diagenetic Study of the Carboniferous Limestone of the Wirksworth Area

3.1 PETROGRAPHY

A detailed petrographic study of the Hoptonwood and Matlock "Groups" shows a variety of fabrics and textures. The study involved the examination of over 200 thin sections, variously stained with Alizarin red-S and potassium ferricyanide to indicate the presence of any dolomite or ferroan calcite (the latter proved negative), and a limited amount of probe analysis using a Cambridge Mk9 Microprobe (Appendix III). The aims of the study were to try and understand the nature of the limestones prior to and after dolomitisation. This may give some information on the factors controlling dolomitisation and the extent to which these factors occur in the original limestone. This may be of prime importance when considering the degree of dolomitisation and whether the different dolostone types are facies related.

The fabrics and textures present in the limestones represent the products of complex diagenetic processes, which transformed very porous, unconsolidated lime mud and sand into an indurated limestone. The main constituents of the fabric of the limestones are the allochems, micrite and sparry cement. These vary in amounts, giving rise to the great variety of limestone types seen in the various quarry sections, (Appendix I). The predominant fragments are arenaceous and this is surprisingly consistent

throughout the limestone succession.

3.1.1. ALLOCHEMS

The most common allochems of these limestones are the crinoid and brachiopod fragments. The crinoid fragments are more abundant in the Hoptonwood "Group" and, although present, are less significant in the Matlock "Group". The crinoidal fragments are mainly ossicles, in many cases, broken and altered due to algal micritisation (pl. 3c), pressure dissolution (pl.3) and later syntaxial rim growth. Syntaxial rim growth may be due to either cavity fill cementation or aggrading neomorphism of the surrounding finely crystalline matrix. Brachiopod fragments are mainly gigantoproductids showing the typical pseudopunctate structure (pl. 2b), These occur predominantly within the Matlock "Group" and are found to form shelly bands which are distinct features of the "Group". Other shell material is indicated by moulds, now filled by a cavity-fill cement. The former shapes of the fragments were retained due to the presence of algal micritisation.

Algae, corals, foraminifera and ostracods also occur quite commonly in these limestones. The algae are particularly abundant in the "Hoptonwood" "Group", giving algal biomicarenites and biosparenites. A number of genera such as Koninckopora (pl. 2a) and Girvanella are present and can also be found coating other fossil fragments (pl. 2c). Corals are represented by rugosa and tabulates. Foraminifera are quite abundant, showing

a number of genera, these are dealt with in greater detail in Section 3.4.

Peloids consisting of a spherical mass of finely crystalline calcite, occur exclusively within the sparenites (Appendix I). Their absence in the micarenites may be due to the difficulty of identification in the finely crystalline matrix. Peloids occur in many of the sparenites in varying amounts and do form distinct beds in the Matlock Group (Appendix I). Ooids are rare and have only been noted close to the Hoptonwood "Group" and Matlock"Group" junction in Middle Peak Quarry. These are well-sorted and usually consist of coated fossil fragments, showing the typical radial calcite, with remnant banding and found exclusively within a sparry matrix. Intraclasts are another allochem present, but these are rare although do form a distinct bed towards the top of Middle Peak Quarry (Appendix I). These can be seen to consist of reworked biomicarenites, which became cemented within sparry calcite.

Geochemically the allochems show a remarkably consistent mineralogy (Table IV), composed essentially of a non-ferroan, low magnesium calcite (0-0.75% $MgCO_3$). Exceptions to this general statement are the crinoidal fragments, which occassionally have slightly higher magnesium values (1.11%). These reflect the former high magnesium mineralogy of the fragments prior to recrystallisation to the now ubiquitous low-magnesium calcite.

3.1.2. MICRITE

Micrite is probably the most abundant constituent of the limestones, and micarenites and microsparenites occur abundantly in the Matlock"Group"and the upper parts of the Hoptonwood"Group". The finely crystalline equant calcite ranging in size from 0-4μm termed micrite (Folk 1965), formed as a result of recrystallisation of an aragonitic/high magnesium lime mud, by either grain growth (Shoji and Folk 1964, rim cementation (Bathurst 1958) or aggrading neomorphism (Bathurst 1971) during early or a late sub-aerial diagenesis, producing a mosaic of low-magnesium calcite.

Although based on a limited amount of data, there is some evidence to suggest that high magnesium calcite may have been a dominant constituent of the former mud. 'High' magnesium values (1.1%) have been found whilst probing the recrystallised mud, suggested by Davies (1977) to be indicative of a former high magnesium calcite.

The origin of the lime mud is not strictly known, however the abundance of algal material may have supplied a significant amount to the muds (Lowenstam and Epstein 1956) together with inorganically precipitated aragonite. The micritic material occasionally found associated with the sparenites may suggest a rock flour, produced by mechanical abrasion of the allochems. Neomorphic aggradation has occurred and caused an increase in crystal size to form

the common microsparenites in the Hoptonwood and Matlock "Groups" (Appendix I).

3.1.3. SPARRY CEMENT

The sparry cement consists principally of a typical drusy cavity-fill cement, increasing the crystal size towards the centre of the former void (Bathurst, 1958). The former voids represent intra- and interparticle pores, and commonly occur between the numerous crinoidal fragments. Here the syntaxial rims tend to completely fill the pores to give a second type of cavity-fill cement (Section 3.2.7). The typical cavity-fill cement tends to be associated with other fossil fragments, intraclasts, peloids and ooids. Intraparticle pores tend to occur in foraminifera, ostracods, corals and a few brachiopods. The spar represents cementation by low magnesium (0-0.9%), non-ferroan cement probably under sub-aerial conditions in the saturated phreatic zone (fig. 3).

3.2. DIAGENESIS

The limestone fabrics have changed considerably during diagenesis in response to many processes, each producing distinctive textures.

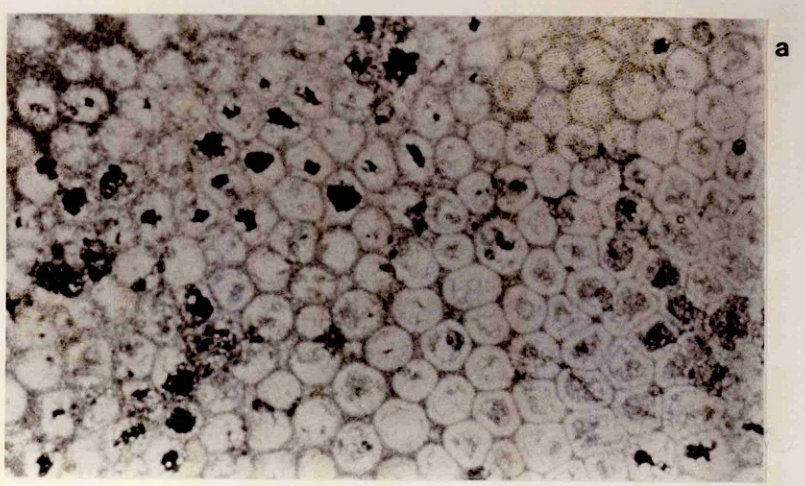
3.2.1. ALGAL MICRITISATION

This term was first introduced by Bathurst (1966) to describe algal boring of allochems, the borings being subsequently filled with finely crystallised aragonite or

Plate 2 Photomicrographs showing various features of the limestone petrography, (a) transverse section of the alga Koninckopora. (b) brachiopod fragment(1) showing the characteristic pseudo-punctate structure,(c),algal material(1) coating an inner shell fragment(2) and(d),algal micritic envelope(1),the inner shell fragment has become dissolved and later filled by a typical cavity-fill cement(2)

Plate 2

a



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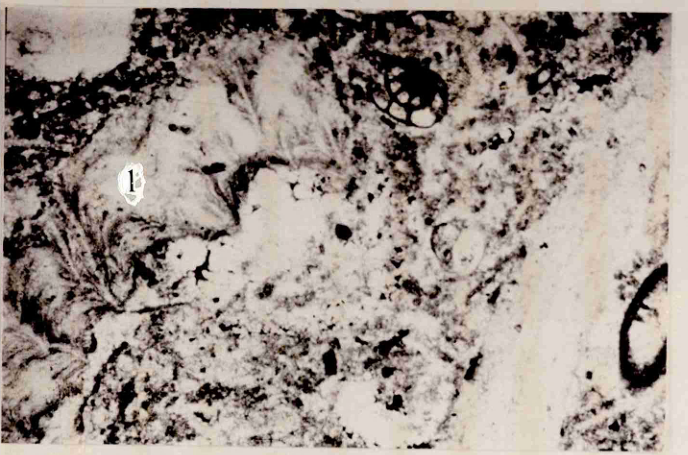

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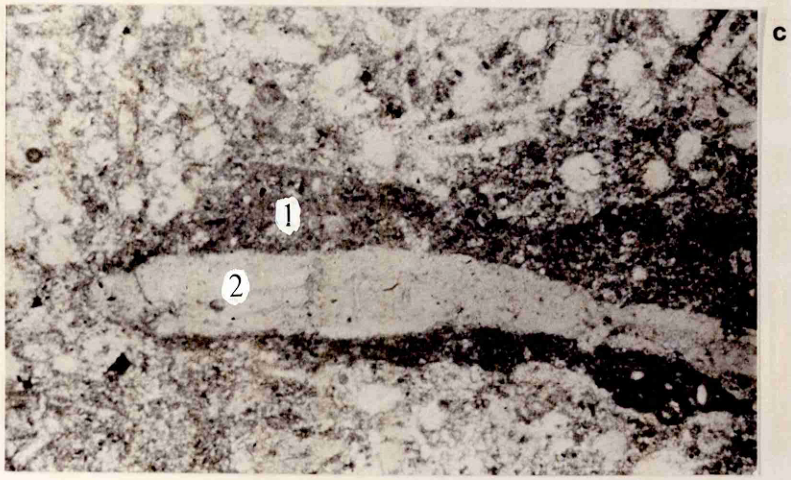

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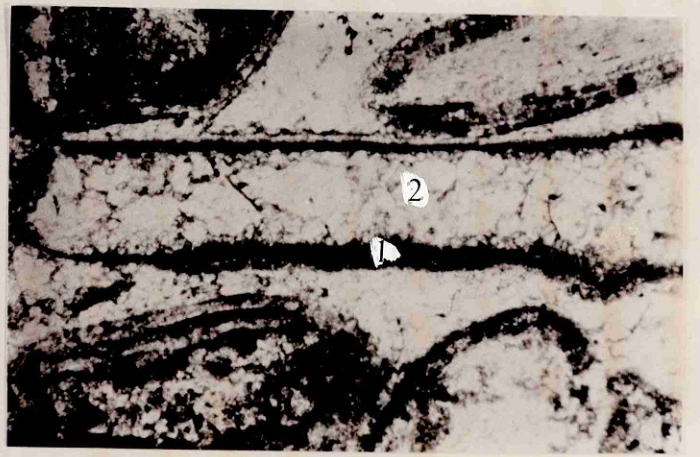

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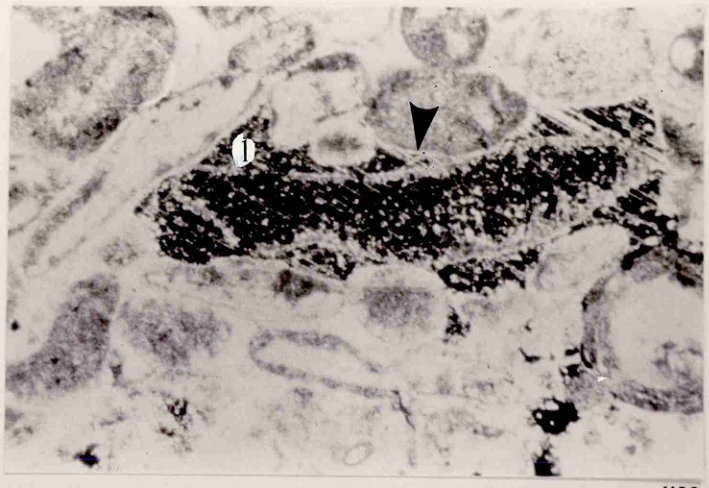
high-magnesium calcite to form a peripheral micritic envelope (Bathurst 1966). Nearly all the biosparenites of this study show extensive micritisation, this is indicated by a very irregular periphery of dark micritic material seen in thin section, using plane polarised light. The abundance of algal material and evidence of algal coated fragments (pl. 2c) suggest an algal origin. An alternative to algal boring was proposed by Friedman et al., (1971), who believe fungal boring can give a similar result. Some fragments have escaped micritisation, these are mainly crinoidal, although micritised crinoidal fragments do occur in the same sample. It seems strange that these have escaped attack, unless the micritised fragments have been transported to the area of deposition and mixed with freshly deposited allochems or alternatively, the few unmicritised fragments may have been introduced to the sediments immediately before burial. Examples of micritised allochems can also be found in the micritic members of the succession.

3.2.2. EARLY CEMENTATION

The interparticle pores of the oosparenites and biosparenites are now filled by a cavity fill sparry cement. The peripheries of some of the allochems in these limestones are marked by a very narrow zone of small furry calcite (pl. 3a). Doubt exists about whether this represents the initial stage of cavity fill cement or an earlier primary cement. The oolitic beds show that ooids coated with an early cement were formed prior to pressure dissolution (pl.3b), which can be shown to be pre-cavity fill

Plate 3 Photomicrographs showing various features of the limestone petrograpgy, (a) crinoidal fragment with the development of a cement syntaxial rim (1),which has developed to fill all the local pore space. Also note the furry periphery to the surrounding allochems, which may indicate a primary cement, (b) pressure solution between an oolith and other allochems the contact is marked by a thin clear calcite(arrow) which may represent a former primary cement,and(c) pressure solution contacts between two crinoidal fragments,the the syntaxial rim being more resistant and therefore protrudes into the other crinoidal fragments.

Plate 3



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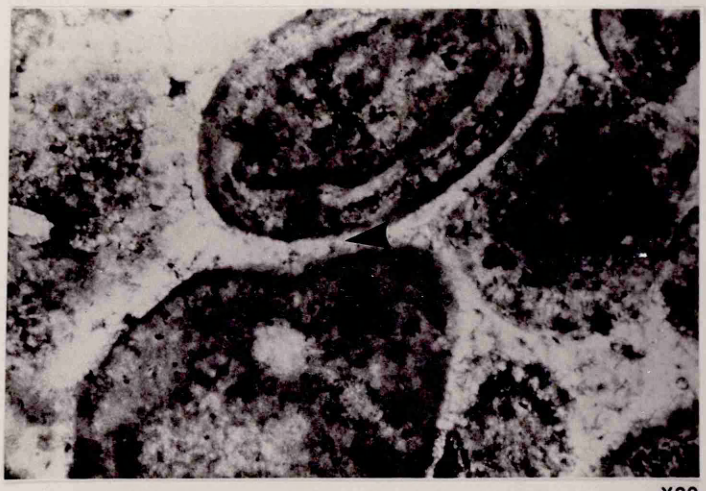

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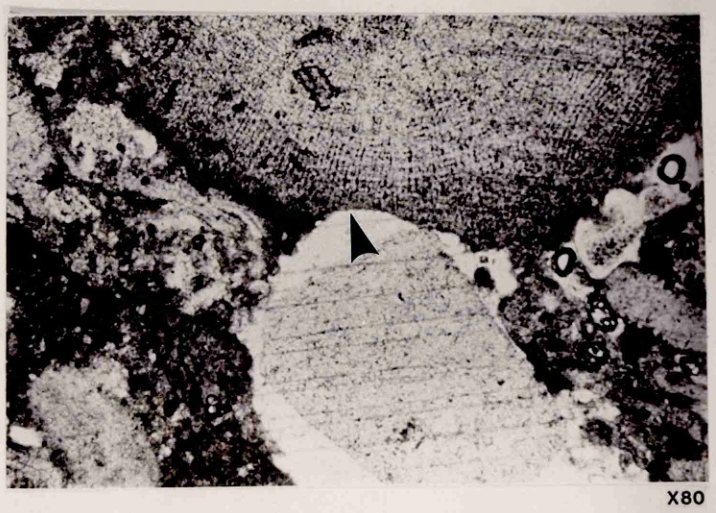

c

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cementation. There (i.e. fig. 3), rimmed ooliths can be seen to impinge upon adjacent ooliths. However, there is some evidence that some of the ooids were in a"plastic state" which, upon compaction of the sediment,became distorted, slipping and fracturing along layers occurring in the more crystalline ooids (pl. 4b). This would allow deformation of the ooids outside the zone of contact, a later sparry infilling around the zone of contact would thus appear to be involved in the deformation , thus suggesting that an early cement did not exist.

The calcite may represent recrystallisation along the zone of contact during pressure dissolution. However, it seems strange that the feature is not ubiquitous.

Where crinoidal fragments are present, syntaxial rims fill the available pore-space, allowing no typical cavity-fill cement to develop. A careful examination of the peripheries of the allochems neighbouring the crinoidal fragments and abutting the syntaxial rim again shows a narrow zone of "furry" calcite. This could be either the development of an early cement or the beginning of a cavity-fill cement before it became inhibited by the expanding syntaxial rim. No evidence of early cementation occuring around the crinoidal fragments is present. This may be a consequence of the late syntaxial rim masking a former cement or the reluctance of the single calcite crystal to promote very fine crystals.

Plate 4 Oosparenite, showing (a) the typical isopachous coating and(b) the fracture of the ooids during compaction(arrow)

The early cement, if it exists, is not ubiquitous and probably represents a poorly developed isopachous marine cement such as described by Ginsburg(1957) and Land (1970). Originally these would be composed of aragonite or high-magnesium calcite, which has become recrystallised to the ubiquitous low-magnesium calcite (Table IV) during later subaerial diagenesis. Due to the minerals' instabilities under these conditions, dissolution may have occurred prior to final cavity-fill cementation. This may explain the sporadic nature of the cement. No geochemical evidence, such as residual high (1.5%) magnesium (Davies, 1977; Marshall and Ashton, 1980), microdolomite inclusions (Lohmann and Meyers, 1977) in calcite, or a replacement by ferroan calcite of former aragonitic or high-magnesium precursor (Richter and Fuchtbauer, 1978), have been found.

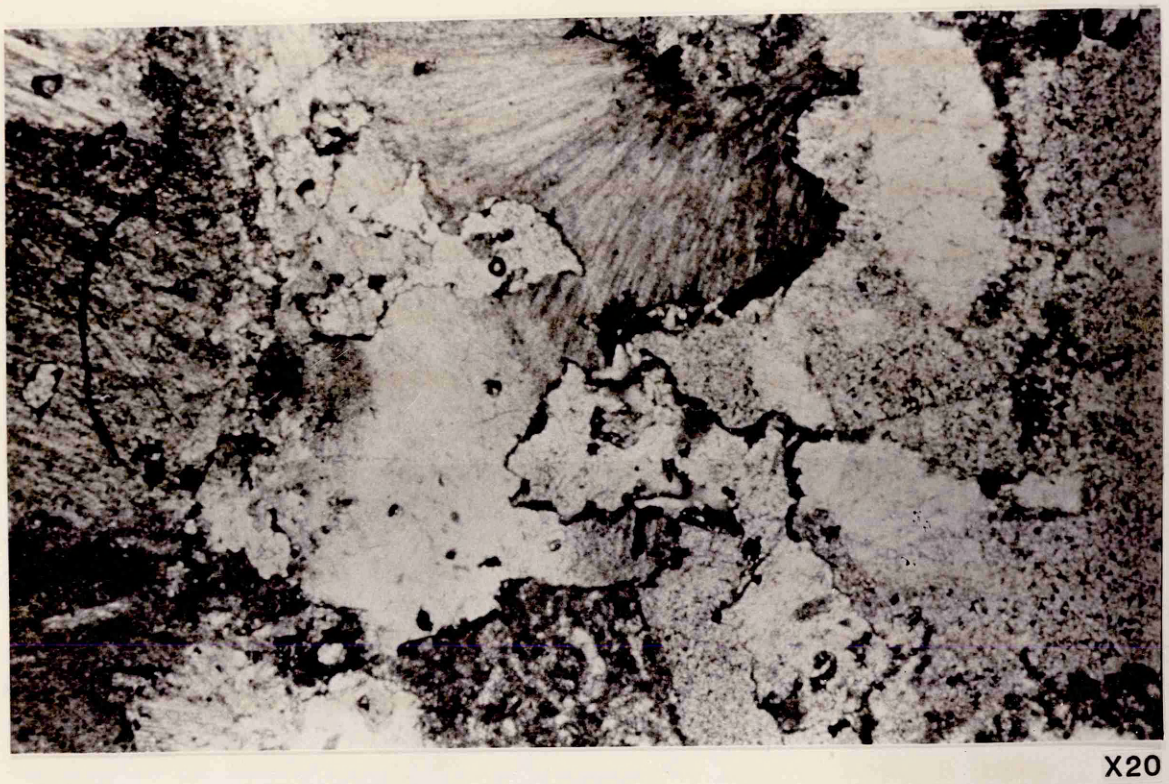
Microprobe analysis has not indicated a definite presence of a former high-magnesium precursor. Although the odd calcite analyses approach 1%, the higher magnesium values are restricted to those phases of calcite believed to have previously been high-magnesium calcite. In this respect, the slightly higher values of the primary cement may indicate a former high-magnesium calcite.

3.2.3. PRESSURE DISSOLUTION

The oosparenites and biosparenites exhibit many pressure dissolution contacts. Prior to compaction, these sparenites formed a self-supporting framework with many grain point contacts. As the load increased, due to

Plate 5 Pressure solution between various allochems, (a) the interdigitation of numerous brachiopod fragments the microstylolitic contacts highlighted by the presence of opaques, either clays or Fe material and(b) protrusion of crinoidal fragment into an adjacent brachiopod fragment

Plate 5



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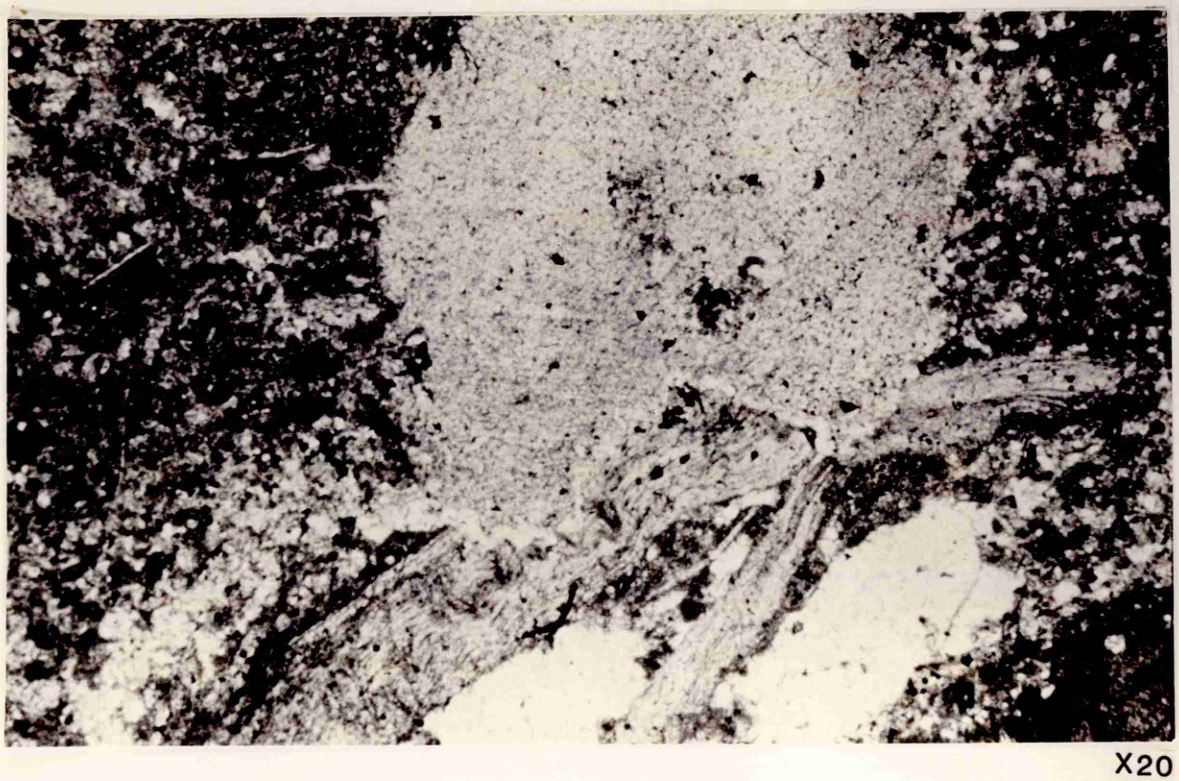

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burial below even a few tens of metres though more usually a few hundred metres (Meyers, 1980), dissolution occurred due to strain at the point contacts and the more soluble strained calcite dissolved and irregular contacts between adjacent allochems developed (Pl. 5b). Similar textures can be seen in a few micarenites, where pockets of allochems occur and micrite is absent, allowing a localised area of self-supporting grains.

The early cement (Sect. 3.2.2), the algal micritisation (Sect. 3.2.1) and some of the syntaxial rims can be shown to be prior to pressure solution (Pl. 3c). The early cement and syntaxial rims tend to be more resistant and protrude into adjacent allochems whilst the micritic envelopes tend to be more soluble and are lost. Pressure dissolution probably occurred reasonably soon after burial and continued to develop into an environment (probably phreatic, Sect. 3.3) where syntaxial rim cementation occurred and prevented any further dissolution.

The most prominent feature of pressure dissolution in field outcrops are stylolites. The majority of stylolites occur in the finely crystalline, more massively bedded and more argillaceous Matlock limestones. A similar association was noted by Manten (1966) in Gotland. They are highlighted in thin section by the occurrence of opaque material, mainly clays and iron oxide lying along the seam. There have been three main origins proposed for stylolites, (1) solution-pressure (Stockdale, 1922, Dunnington, 1954), (2) contraction-pressure (Shaub, 1939) and (3) a seafloor origin (Prokopovich

1952). The more widely accepted origin is the dissolution-pressure idea, and debate has now moved to the time of origin i.e. whether pre- or post-induration.

The stylolites of this study are believed to be a result of a dissolution-pressure process, due to the extreme interdigitation of adjacent fossil fragments (pl. 5a). The controlling factor is the orientation of the axis of linear stress and this is generally vertical, being a simple consequence of overburden. The zig-zag form of the surface is presumed to be a consequence of lateral variations of solubility, along the interface. Where a more soluble crystal confronts a less soluble part across a solution film, then the most soluble part will dissolve. Where grains have different solubilities, one may dissolve more rapidly than the other, to form very irregular interfaces. Although a limited number of samples were studied in thin section, there is a very strong suggestion that many of the more sparry areas, eg. allochems, if affected by the stylolitisation, form the more resistant columns of the stylolites. A similar occurrence was noted by Bathurst (1971, p.470). Examples can be seen where microsparite, caused by aggrading neomorphism seems to form the more resistant columns, suggesting that stylolitisation was contemporaneous with, or later than induration. It is presumed (Dunnington, 1954, Bathurst, 1971) that stylolitisation ceases when the permeability falls so low, as a result of cementation, that the transport of ions away from the solution film is inhibited. It would seem that stylolitisation

occurred contemporaneously or towards the end of cementation (fig. 4).

3.2.4. AGGRADING NEOMORPHISM

The Matlock "Group" consists predominantly of finely crystalline limestones with varying amounts of allochems, which occur to a lesser extent in the Hoptonwood "Group". The finely crystalline matrices range in size from 2-4 μm but have isolated areas of microsparite up to 200 μm across which when well developed give rise to "pseudobreccias". These are believed by Folk (1965) to develop by aggrading neomorphism, namely the coalescence of adjacent calcite crystals in the presence of a fluid phase.

Schlanger (1964) found that similar structures in the Tertiary Limestones of Guam, West Pacific, begin in a partly consolidated sediment during the transformation of aragonite to calcite, although many believe the process to be an indication of later diagenesis, being due to recrystallisation of the lime mud/micrite, possibly initiated by stress. The process was previously described by Bathurst (1958) and Orme and Brown (1963) in the British Dinantian Limestones and postulated as being due to grain growth i.e. an anhydrous recrystallisation (solid state), similar to the process found in metallurgy. The driving force for this is believed to be differences in surface tension and application of directional stress, which will have a great part to play in Folk's hypothesis. Bathurst (1971), later repudiated this

anhydrous origin and stated that the mechanism proposed by Folk involving a fluid phase was more likely.

Alternative origins for the microsparenites are that (1) they represent cavity-fill calcite and (2) they are silt-size allochems. There is no evidence to suggest a cavity-fill origin, such as sharp boundaries, in fact these are gradational and in some cases include areas of former micrite. It is doubtful that they represent smaller allochems, as no evidence exists of biological structures in any of these areas.

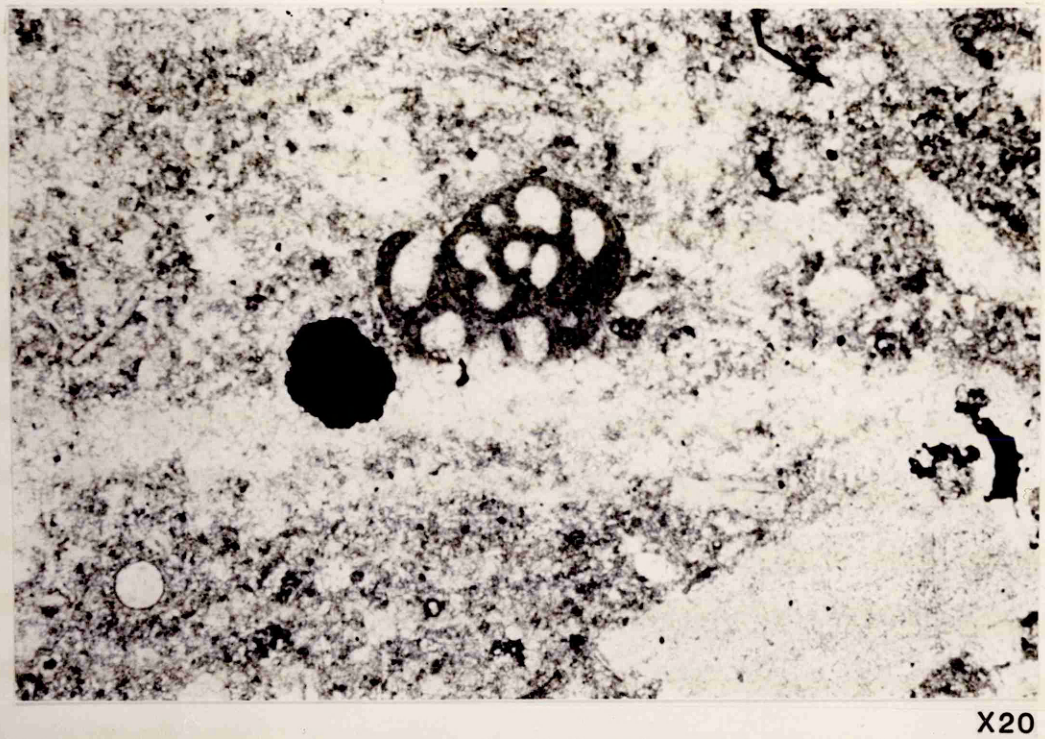
Where the recrystallisation is found to be extensive and abutting fossil fragments, most fragments remain unaltered although the more finely crystalline fossils, such as foraminifera and to a certain extent finely crystalline shell fragments are slighted affected (pl. 6a) similar observations were made by Banner and Wood (1964).

3.2.5. REPLACEMENT

The inversion of the lime mud to a uniform micrite has been discussed (Sect. 3.1.2), but no positive indication of its predecessor can be found. On the other hand, the allochems show good evidence of replacement. The predominant fossil fragments present are crinoidal and shelly. The crinoidal fragments have remained as single crystals even though a possible mineralogical change from high-magnesium calcite to low-magnesium calcite (Table IV) seems to have occurred.

Plate 6 Recrystallisation of (a) the micritic matrix causing the destruction of a foraminifera and (b)a shell fragment by a coarse fibrous calcite,yet retaining a ghost of the former layering(arrow) of the shell.

Plate 6



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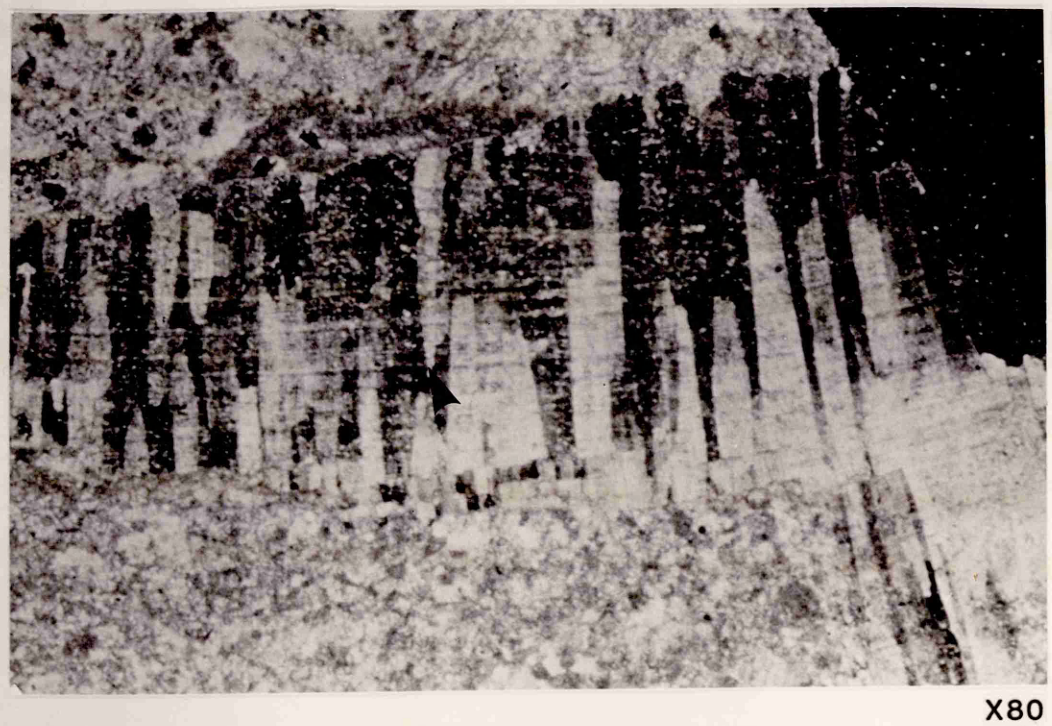

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The shelly fragments are mainly brachiopodal and these have suffered little obvious alteration, as the fibrous, prismatic and microcrystalline textures have been retained, these are believed to be productid fragments, in many cases showing a pseudo-punctate structure and development of spine bases. Other shelly fragments however, have suffered a very clear recrystallisation, which may reflect their original mineralogy. Plate 6b shows a shell fragment replaced by a radiaxial calcite, although retaining the original banding, perpendicular to the radiaxial calcite. The replacement probably occurred, not by grain-growth, but with a fluid phase present along a narrow front, the neomorphic calcite gradually transgressing the shell. The narrow zone of dissolution-precipitation as described by Bathurst (1971) allows inclusions to remain in very similar positions to those in the original shell and thus retain a ghost of the original shell structure. A similar process may be involved with the previously described brachiopod fragments, except that aggradation occurred to a much lesser extent. Plate 2d shows a classic micrite envelope which resisted dissolution, probably under subaerial conditions. The inner remains of the shell fragment becomes dissolved and the void (maintained by the micritic envelope) later became filled with a cavity-fill cement.

The different types of replacement probably represent differing original mineralogies. A recrystallisation in a

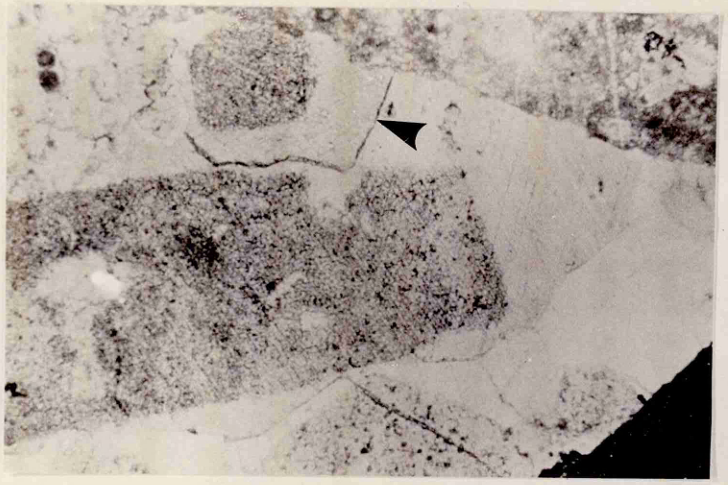
fluid media is involved, as a solid state inversion of aragonite to calcite seems unlikely under saturated phreatic conditions. The brachiopodal fragments, although possibly having a fairly high-magnesium content, suffered little recrystallisation. Other shelly fragments were probably composed of more soluble calcium carbonate such as high-magnesium calcite or aragonite. The shells which were completely dissolved were probably the more soluble aragonite.

3.2.6. CAVITY-FILL CEMENTATION

The sparenites are cemented by a typical cavity-fill drusy sparry cement (pl 7d), increasing in crystal-size towards the centre of the interparticle pores (Bathurst 1958). The spar filled the modified pores, which remained after the initial compactional pressure dissolution. It is not exclusive to the sparenites, as some shelter porosity and other interparticle porosity does occur in the micarenites. Other occurrences of the cement, are filling intraparticle pores of foraminifera, ostracods, corals and some brachiopods. Geochemically the cement is typical of a subaerial (phreatic) cement, consisting of low-magnesium calcite with little iron or manganese (Table IV). According to Longman (1980) these cements are indicative of a saturated active phreatic zone which under suitable conditions could deposit such cements.

Plate 7 Various types of cement occurring in the limestones (a) cement syntaxial rims(arrow) (b) irregular neomorphic syntaxial rim(arrow),(c) crinoid fragment showing algal micritisation (arrow) and probably grain diminution and (d) a typical cavity -fill cement

Plate 7



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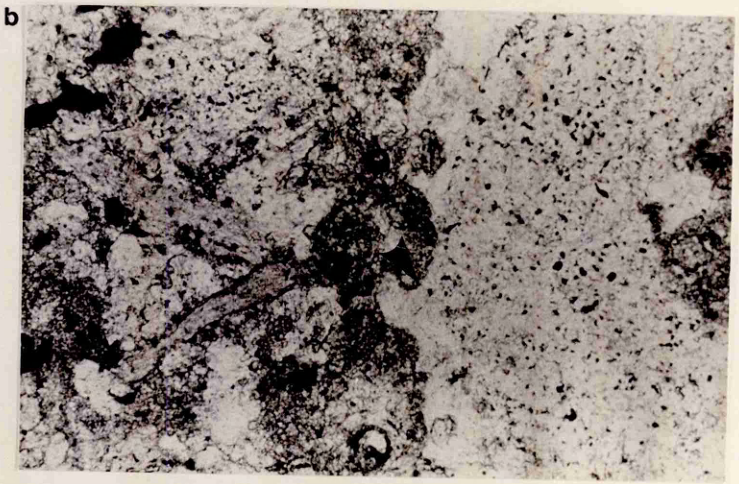

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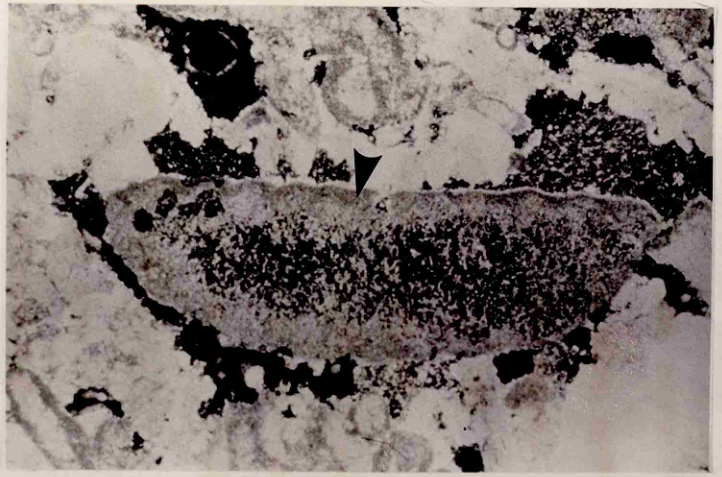

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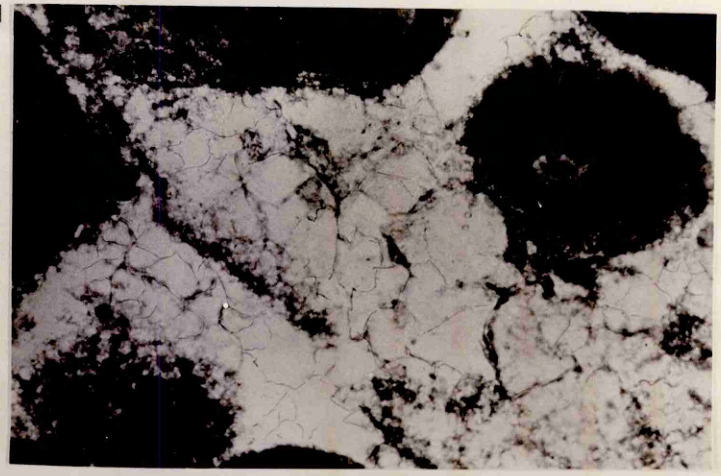

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suggests that the meteoric component of the phreatic zone was dominant (fig. 3). constantly supplying well oxygenated water to the site of deposition. An enigma of this type of cement is the great amount of calcium carbonate required for its origin (Bathurst, 1971). Two sources are suggested (1) that some of the calcium carbonate was derived from pressure solution and (2) that the majority of the calcium carbonate was derived by solution of carbonate material in the vadose and aggressive upper phreatic zone, lying above the zone of deposition (fig. 3).

3.2.7. SYNTAXIAL RIM DEVELOPMENT

Syntaxial rims predominantly occur associated with crinoid fragments. The rims can be divided into two types, (1) cement syntaxial rims occurring mainly in the sparenites, filling the available interparticle pore space (pl. 3a) and (2) replacement syntaxial rims occurring exclusively in the micrite members of the succession and are due to aggrading neomorphism. In both cases, the inner original crinoidal fragments are distinguished by the abundance of impurities probably clay, iron oxide or fine-grained calcium carbonate (less likely, as these will have become recrystallised), filling the original micropore structure of the crinoid fragments. The rims are identified by their inclusion-free nature and optical continuity. Both rims have a similar chemistry (Table IV) and show no internal chemical variation as found by Evamy and

Shearman (1965), suggesting a marine origin. The cement syntaxial rims (pl. 7a) are cavity-fill sparry cement and usually completely fill the available adjacent interparticle pore space, except for the presence of an early cement (Sect. 3.2.2). Lucia (1962, p.851) noted that the rate of growth of syntaxial rims is greater than that for drusy cements, explaining the textures seen in these samples. No evidence, such as microdolomite inclusions (Meyers and Lohmann, 1978), residual higher magnesium content (Davies, 1977), to suggest that such cements may have a marine or mixed marine/fresh origin can be seen.

Microprobe analysis has shown the cement syntaxial rims to be chemically uniform, consisting of a low-magnesium calcite with virtually no iron or manganese. They show a very similar chemistry to the remainder of the limestone and in particular to the cavity-fill cement.

This is not taken as being conclusive of a former high-magnesium calcite being present. It is accepted that magnesium can be lost during recrystallisation. However, it is believed that these have a similar origin to the cavity-fill cement i.e. within the active phreatic zone, and do not represent an earlier high-magnesium calcite.

As mentioned (Sect. 3.2.1) many of the allochems in the sparenitic beds are extensively micritised. There are examples to show that where crinoidal fragments are extensively micritised, the micrite envelopes inhibit

the growth of a syntaxial rim. However, there are fragments which appear badly micritised, but still allow the growth of a rim. It is suggested that these particular rims have a similar explanation to those found by Evamy and Shearman (1965). They found that unless the micritisation completely surrounds the fragment, it does not inhibit the formation of the rim.

The replacement syntaxial rims occur exclusively in the micritic members of the succession. The rims grow in optical continuity away from the crinoidal fragments by means of aggrading neomorphism (Bathurst 1971), gradually replacing the surrounding micrite and forming very irregular peripheries to the rim (pl. 7b). A replacive nature is suggested by the very irregular nature and the ill-defined boundary with the micritic matrix. The neomorphic rims seem isopachous, which contradicts the type of origin suggested by Evamy and Shearman. It is accepted that some rims may have had a marine or brackish origin and have gone through a complex diagenesis to give a similar chemistry to those rims believed to be of subaerial origin. Geochemically, the neomorphic rims of this study are very similar to the cement rims and the original micrite (Table IV). In the absence of any evidence of a marine origin, suggested by Evamy and Shearman, for similar rims (they believed these to have formed as primary rims on the sea floor and not a replacive origin), the rims are believed to have a subaerial origin, possibly originating at an early stage.

in the rocks' diagenesis, occurring contemporaneously with the aggrading neomorphism of the matrix.(Sect. 3.2.4).

As stated earlier, syntaxial overgrowths are not exclusive to the crinoidal fragments and within the Matlock Group, small syntaxial overgrowths occur on some shelly fragments. These seem to occur associated with the more coarsely crystalline shell fragments, and are believed to be neomorphic, being very similar to those described by Bathurst (1971 p. 492).

3.2.8. GRAIN DIMINUTION

The grain diminution of the crinoid fragments which is so common in the dolomite pseudomorphs of the dolostones (Munn and Jackson 1980), occurs only rarely in the unaltered limestones. Where it exists, it is most evident in the crinoidal fragments (pl.7c), due to their large crystal size. These areas of micritic calcite enclosed within a large crystal differ from the algal or fungal micritisation described earlier (Sect. 3.2.1) in that, these are not represented in plane polarised light by a darkened mass of micrite and are not usually peripheral. This diminution is very similar to that described by Voll (1960), Wardlaw (1962) and Orme and Brown (1963), which was proposed to be due to an "in situ" replacement of a deformed crystal by cryptocrystalline unstrained crystals, caused by the application of stress, possibly compactional. Lucia (1968), Alexandersson (1972) and Neugebauer (1978) have shown the process could

be early diagenetic caused by a selective dissolution during a mineral transformation from high to low-magnesium calcite. These textures resemble the micritic envelopes of Bathurst (1966), which may have a great influence upon the process during stress. Caution must be taken, following Towe's (1967) work, where he showed crinoidal crystals to be, at least in part, composed of a multitude of tiny crystals, near the growing edge, having a similar optical orientation. This explanation seems unlikely for the features seen in the limestones of this study, due to the great abundance of grain diminution in some beds and complete lack in others.

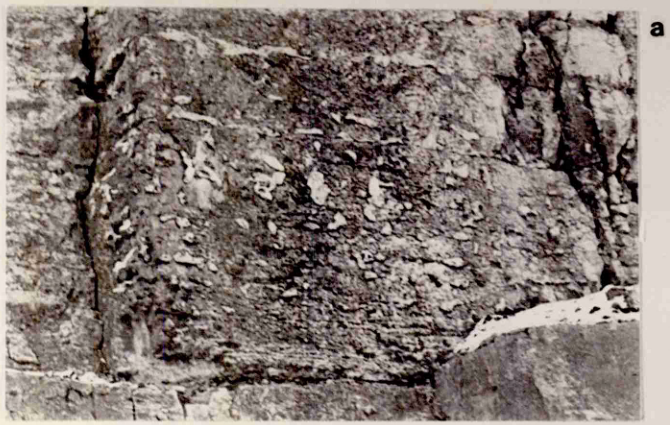
3.2.9. SILICIFICATION

Cherts occur mainly in the upper parts of the more thinly bedded and argillaceous Matlock and Cawdor "Groups". This finding has also been noted by Sargent (1921) elsewhere in Derbyshire. These occur as nodular or tabular bodies, usually parallel to bedding, although occasionally occur within beds and are clearly secondary (pl. 8a). Where the limestone is totally silicified, the silica can be seen to have pseudomorphed the various crystal sizes and shapes constituting the fabric (pl. 8b). Exceptions to this are the crinoid fragments, which appear more resistant to silicification and retain a calcite core (pl. 8c). The replacement is not pseudomorphic, as the large calcite crystals are partially replaced by spherulitic chalcedony. Some crinoidal fragments show a cryptocrystalline rim of silica, this probably represents

Plate 8 Various features of the silicification of the limestones; (a) nodular and tabular chert from the Cawdor "Group", Intake Quarry (b) total silicification of limestone matrix and brachiopod fragment, showing mimicing of microsparite; (c) spherulitic silica beginning to replace crinoidal fragment, but only seeming to replace the peripheral micritic rim; and (d) preferential silicification of brachiopod fragments.

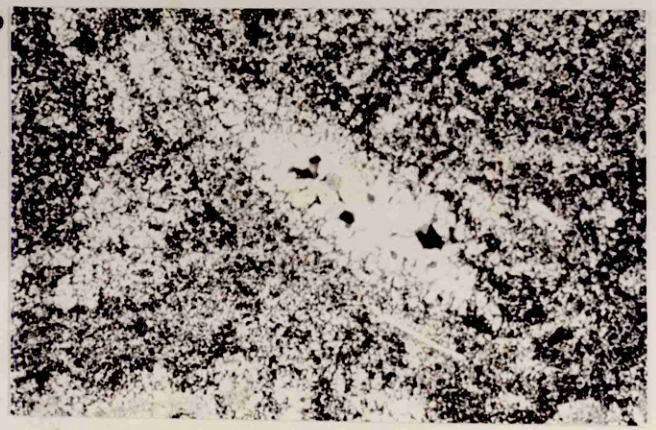
Plate 8

a



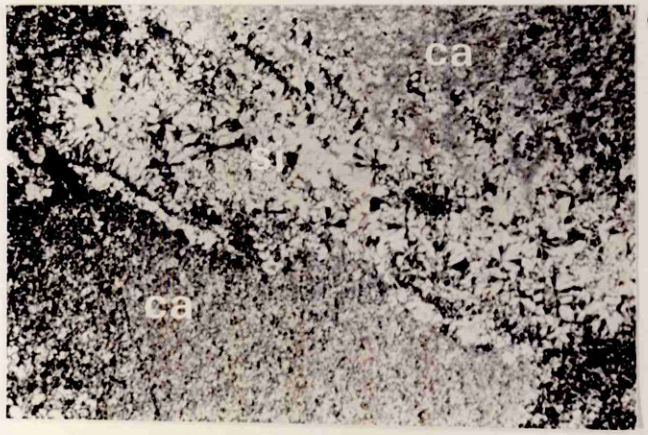
30cms.

b



X20

c



X80

d

X80

a silicified micritic envelope (pl. 8c). The silicified matrix consists of a microcrystalline silica (after micrite) with isolated areas of slightly larger crystals. These could represent a replacement of a microsparite calcite formed by aggrading neomorphism, and may suggest that silicification is post-early diagenesis. Initially, silica appears to preferentially replace brachiopod fragments evidenced by the many isolated totally silicified brachiopod fragments in some limestones (pl. 8d), also noted by Milner (1976). Thus, the most susceptible allochems appear to be the brachiopod fragments, continuing silification would cause the replacement of the fine-grained matrix, together with other microcrystalline fossil material, the crinoid fragments remaining fairly resistant due to their crystal size.

The insoluble residues of limestones from both the Hoptonwood and Matlock "Groups" contain numerous small euhedral bipyramidal quartz crystals (100-200 μm). In the sparenites, these can be shown to cut across cavity-fill structures, indicating their later origin. Within a dolomitised bed of the Matlock "Group" seen at Intake Quarry, total silicification of the cavity-fill calcite of the rhombohedral pores, formed during dolomitisation, has occurred. If, these two occurrences of silica are related to the major phase of silicification, then the cherts are clearly late diagenetic.

The origin of the silica is unknown, there is no

great abundance of sponge spicules, although they are present, however the cherts are associated with the more argillaceous beds and the clays, which may act as a source for silica. The occurrence of many volcanic rocks in the area may also be significant as a source for the silica - a suggestion made by Sargent (1921). In this area of study the Lower Matlock Lava now represented by a clay, must have released considerable amounts of silica.

3.3. DIAGENETIC EVOLUTION OF THE CARBONIFEROUS LIMESTONE IN THE WIRKSWORTH AREA

The early diagenesis of the limestones appears to have begun in a marine environment, with algal and/or fungal activity producing heavily micritised allochems. This probably occurred very close to the water-sediment interface (Kobluk and Risk 1977) and under these conditions became lightly cemented by an isopachous early cement. Pressure dissolution most evident in the sparenites, began after burial due to compaction and continued during early subaerial diagenesis, whilst the rock remained reasonably uncemented. The above features are to be found in the sparenites. The more micritic beds show very few signs of marine diagenesis, although many of the features of the micrites associated with the subaerial environment, such as aggrading neomorphism, may have marine beginnings.

After the initial marine diagenesis the limestones appear to have moved into a subaerial environment, either

eustatically or isostatically. The environment is dominated by the influence of meteoric waters, and due to the instability of high-magnesium calcite and aragonite in this environment, and the low magnesium/calcite ratio of the waters, stabilisation of the carbonate phase to low magnesium calcite began. Some of the textures, such as cavity-fill and to a certain extent cement syntaxial rims are indicative of this type of environment. Aggrading neomorphism and recrystallisation of the matrix and allochems, although not entirely restricted to this environment, do appear to be predominant features of these conditions, in these limestones (fig. 4).

Basically, the subaerial environment can be divided easily into; (1) the vadose zone, and (2) the totally saturated phreatic zone. The limestones show no evidence of vadose diagenesis, such as extreme dissolution, meniscus or capillary cements. Most of the textures in this study appear to have formed under phreatic conditions. Ideally, the phreatic zone can be divided into four important zones (Fig.3) (Longman 1980), each important in the development of the many textures of the limestones. Of course, the development and extent of these various zones are controlled by many variables (such as relief, climate, tectonics and lithology).

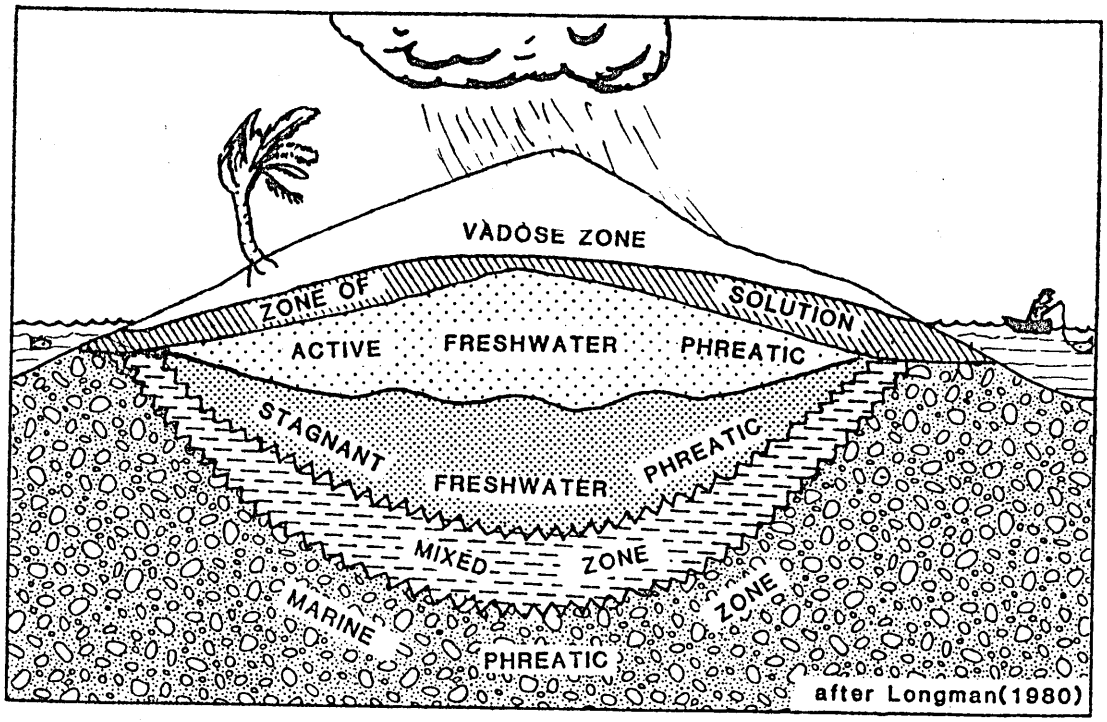


Figure 3 Idealised diagram of the various groundwater zones

(1) a zone of solution - here undersaturated meteoric water reaching the top of the phreatic zone, is still capable of dissolution and thus mouldic vugs may develop. Under very localised conditions some dissolution - precipitation may occur.

(2) an active freshwater zone - lying below the zone of solution, percolating waters having become saturated, will begin to deposit calcium carbonate to form the typical cavity-fill cements and cement syntaxial rims. Deposition of calcium carbonate is caused by either the decrease in carbon dioxide or rise in temperature. The waters, although saturated with respect to calcite, may remain undersaturated with repect to aragonite or high-magnesium calcite and can again cause replacement.

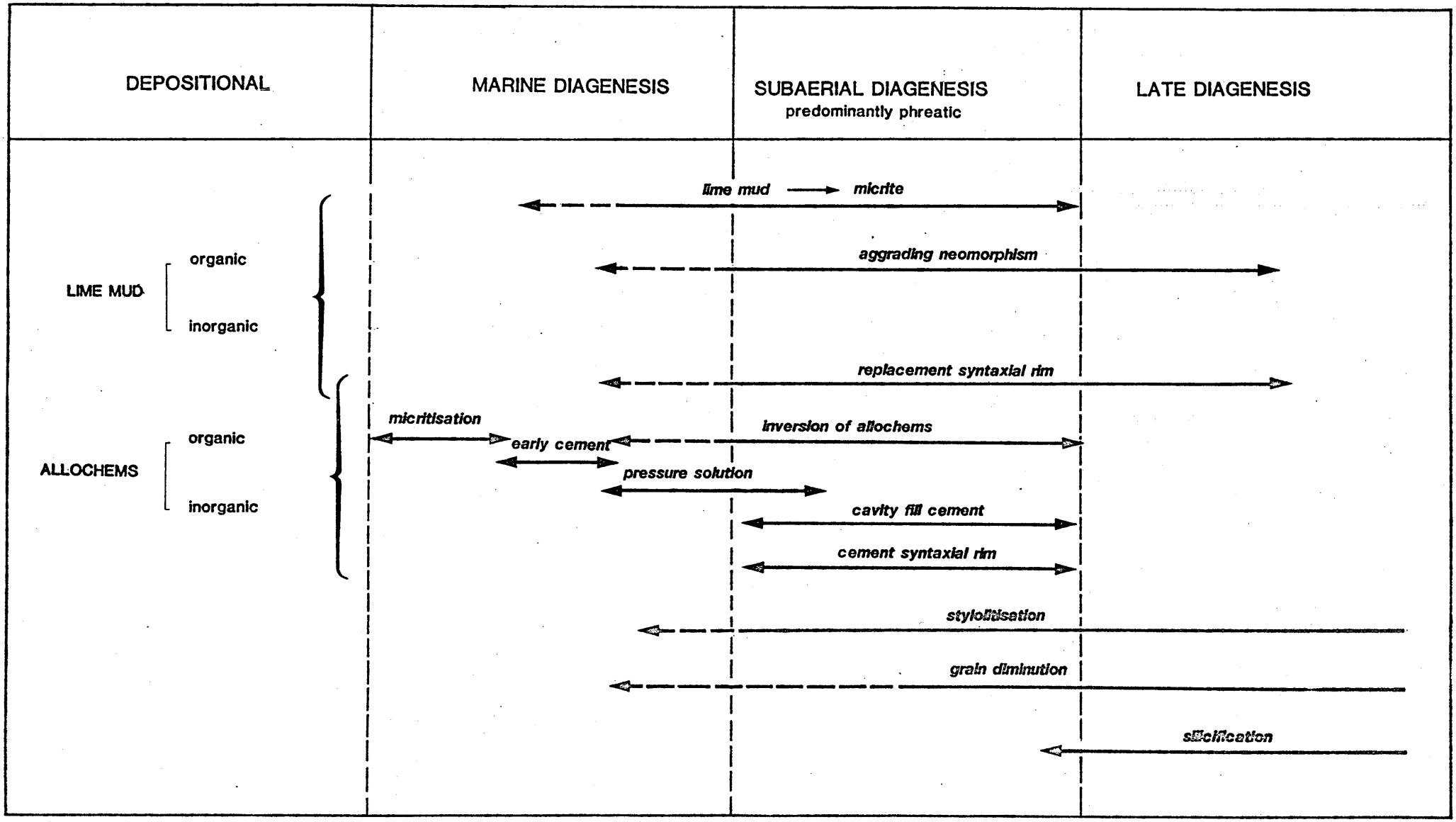


Figure 4 A summary of the various stages of diagenesis found in the Carboniferous Limestone of the Wirksworth Area

(3) a stagnant freshwater zone - although saturated with respect to calcite, there is little water movement and thus little cementation will occur. Longman believes that under these conditions stabilisation of aragonite and high-magnesium calcite (lime mud and allochems) can occur with preservation of the original textures (Section 3.2.5). Processes occurring under these conditions, together with compactional stress may be a great driving force for aggrading neomorphism, occurring contemporaneously with the recrystallisation of the mud and allochems. Similar processes in the first two zones would probably cause complete dissolution and later infilling by a cavity-fill cement.

(4) a mixed freshwater and marine zone - here, there is a mixing of marine and meteoric waters, which under certain conditions may be dominated by one or the other. This leads to a variety of conditions and thus a variety of textures. No evidence of this environment was found in the limestones of this study.

It can be seen that the freshwater phreatic zone could provide the necessary conditions to produce the great majority of the textures seen in the Hoptonwood and Matlock limestones (fig. 3). The limestones are also chemically consistent in that low-magnesium is indicative of a meteoric environment. The low iron and manganese may indicate the dominance of the meteoric component of the phreatic zone, over more stagnant connate water, thus constantly supplying well-oxygenated water even within the stagnant zone. There is ample evidence

throughout Lower Carboniferous Limestone times, to suggest that several sea level changes occured (Ramsbottom 1973 and Sommerville 1979). Walkden (1970) has noted a similar change in the Asbian and Brigantian stages of the Lower Carboniferous Limestone in Derbyshire. The lowering of sea level is marked by the development of clay wayboards and associated palaeokarstic surface. Thus, there seems to have been ample opportunity for the subaerial stabilisation and induration of the limestone to have occurred during Lower Carboniferous times, quite soon after deposition.

Late diagenetic features, some occurring probably at depth below Middle and Upper Carboniferous sediments, are rare. These may include silicification, stylolitisation and grain diminution, although these may also have an earlier origin. The most important late diagenetic feature of the area is dolomitisation.

3.4. Foraminifera

The study of the foraminiferal fauna involved the careful examination and photographing of over 100 thin sections. Thirty eight taxa have been identified and these are listed in Appendix II. Plates 9-13 show many of the genera and species present. The foraminifera seen in these plates are not representative of the limestones sampled because they represent the better preserved specimens.

Magnification of each plate is x75.

Plates 9 and 10. - Hoptonwood Quarry

1. Earlandia sp.
   H.W. 22 (Appendix II), Hoptonwood "Group", Asbian.

2. Forschiinae sp.
   H.W. 22 (Appendix II),Hoptonwood "Group",Asbian

3. Koskinobigerina sp.
   H.W. 22 (Appendix II),Hoptonwood "Group",Asbian
   Remarks: No inner fibrous layer,although may have been lost during diagenesis.

4. Earlandia sp.
   H.W. 22(Appendix II),Hoptonwood "Group",Asbian.

5. Plectogyranopsis sp.
   H.W. 22(Appendix II),Hoptonwood "Group", Asbian
   Remarks: similar irregular inner whorls and lobate later whorls to Endothyra ,but distinguished by it's wall structure and rapid increase in whorl size.

6. cf. Georgella sp.
   H.W. 22 (Appendix II),Hoptonwood "Group",Asbian.
   Remarks: shows similar iniserial terminal portion to Mikhailovella but does not show internal septae or cribrae. Thes may have been lost during diagenesis.

7. Mikhailovella sp.
   H.W. 22(Appendix II),Hoptonwood "Group",Asbian.
   Remarks: see plate 9(6)

8. Archaediscus varsanofievae (Grozdilova and Lebedeva 1954)
   H.W. 26(Appendix II), Matlock "Group",Brigantian.

9. Archaediscus varsanofievae (Grozdilova and Lebedeva 1954)
   H.W. 26(Appendix II),Matlock "Group",Brigantian.

10. Endotyra sp.
    H.W.25 (Appendix II),Matlock "Group",Brigantian.
    Remarks: description of Endothyra is vague and can vary from almost planispiral to irregularly coiled throughout,thus sample may represent inner whorls of Eostaffella.

11. Endothyra sp.
H.W.26(Appendix II),Matlock "Group",Brigantian.

12. Archaediscus varsanofievae (Grozdilova and Lebedeva 1954)
H.W. 26(Appendix II),Matlock "Group",Brigantian.

13. Archaediscus sp.
H.W. 25 (Appendix II),Matlock "Group",Brigantian.

14. Archaediscus grandiculus (Schlykova 1951)
H.W. 26(Appendix II),Matlock "Group",Brigantian.

15. Archaediscus sp.
H.W. 28 (Appendix II),Matlock "Group",Brigantian.

16. Loeblichidae sp.
H.W. 25 (Appendix II),Matlock "Group",Brigantian.
Remarks: very similar to Endostaffella

19. Bradyina rotula (Eichwald 1860)
H.W. 28 (Appendix II),Matlock "Group",Brigantian.
Remarks: showing characteristic perforate wall.

20. Endothyranopsis sp.
H.W. 28 (Appendix II),Matlock "Group",Brigantian.

21. Cribostomum cf. lecompti (Conil and Lys 1964)
H.W. 28 (Appendix II),Matlock "Group",Brigantian.
Remarks:characteristic inner fibrous wall and inflated septal ends.

22. Palaeotextularia sp.
H.W. 26 (Appendix II),Matlock "Group",Brigantian.
Remars: characteristic inner fibrous wall an biserial form. Similar to Cribostomum but unlikely to a different angle of section of Cribostomum due to the overlap of the septa in this sample.

23. Koskinotextularia sp.
H.W. 24 (Appendix II),Matlock "Group",Brigantian.
Remarks: very similar to Cribostomum apart from the fibrous inner wall,which could be lost during diagenesis.

24. Endothyranopsis cf. crassa(Brady 1876)
H.W. 27 (Appendix II),Matlock "Group",Brigantian.

PLATE 9

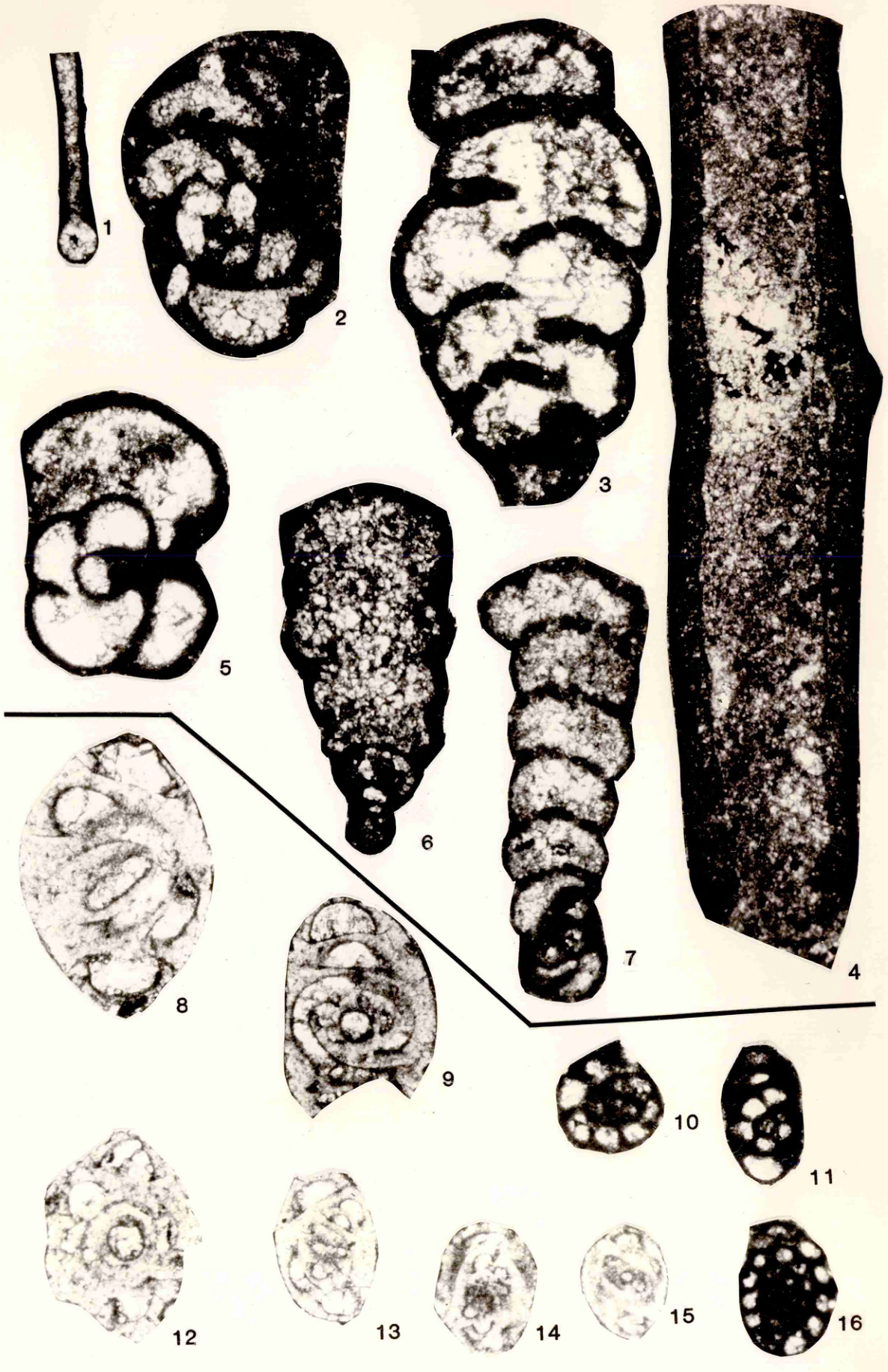


PLATE 10

19

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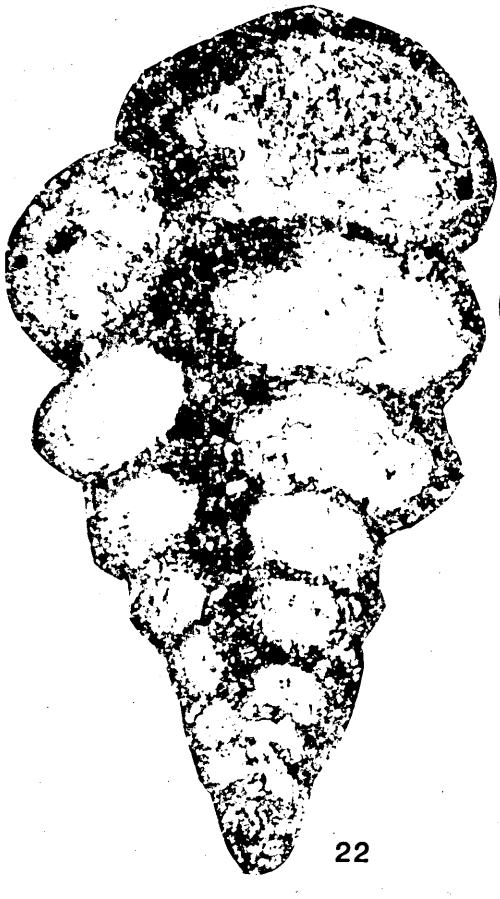
21



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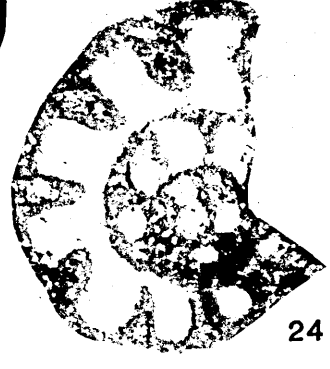
23



24

Magnification for each plate x75

Plates 11 and 12.- Middle Peak Quarry

1. Endothyra sp.
BL5 (Appendix II),Hoptonwood "Group",Asbian.

2. Tetrataxis conica (Ehrenberg 1854)
$L_1$5 (Appendix II),Hoptonwood "Group",Asbian.

3. Endostaffella sp.
$L_2$3(Appendix II),Hoptonwood "Group",Asbian.

4. Pseudoendothra cf.sublimis (Schlykova 1951)
$L_2$8 (Appendix II),Hoptonwood "Group",Asbian.
Remarks: characteristic sharp keel.

5. Palaeotextularia sp.
$L_2$3 (Appendix II),Hoptonwood "Group",Asbian.
Remarks: characteristic inner fibrous wall,similar to Cribostomum apart from fused nature but is unlikely to be due to the angle of section as the septa overlap.

6. Mikhailovella sp6
$L_2$7 (Appendix II),Hoptonwood "Group",Asbian.
Remarks: shows development of cribrae.

7. Eostaffella sp.
$L_2$5 (Appendix II),Hopton.wood "Group",Asbian.

8. Millerella sp. (Thompson 1942)
L_2? (Appendix II),Hoptonwood "Group",Asbian.
Remarks: similar to Eostaffella but more laterally compressed with marked blunt ends.

9. Endostaffella sp.
$L_2$5 (Appendix II),Hoptpnwood "Group",Asbian.
Remarks: another small almost planispiral form,similar to many other genera,particularly the inner whorls of Eostaffella.

10. Eostaffella cf. mosquensis (Vissarionova 1948)
$L_2$5 (Appendix II),Hoptonwood "Group",Asbian.

11. Plectogyranopsis sp.
BL5 (Appendix II), Hoptonwood "Group",Asbian.
Remarks: shows many similarities to Endothyra except for thicker outer wall.

12. Archaediscus varsanofievae (Grozdilova and Lebedeva 1954)
$L_3$5 (Appendix II),Matlock "Group", Brigantian.

13. Archaediscus convexus (Grozdilova and Lebedeva 1954)
$L_4$1 (Appendix II),Matlock "Group",Brigantian.

14 Archaediscus sp.
$L_3$6 (Appendix II),Matlock "Group",Brigantian.

15. Archaediscus varsanofievae (Grozdilova and Lebedeva 1954)
$L_3$3 (Appendix II),Matlock "Group",Brigantian.

16. Archaediscus stilus (Grozdilova and Lebedeva 1954)
$L_4$1 (Appendix II),Matlock "Group",Brigantian.

17. Nodoarchaediscus sp.
$L_4$7 (Appendix II),Matlock "Group ",Brigantian.
Remarks: apperrance of nodes in outer whorls,which is not very clear in plate.

18. Pseudoammodiscus cf. nudus (Malakhova 1963)
$L_6$2 (Appendix II),Matlock "Group",Brigantian.

19. Eostaffella sp.
$L_3$7 (Appendix II),Matlock "Group",Brigantian.

20. Eostaffella cf. mosquensis (Vissarionova 1948)
$L_4$4 (Appendix II),Matlock "Group",Brigantian.

21. Eostaffella cf. parastruvei (Rauser 1948)
$L_4$4 (Appendix II),Matlock "Group",Brigantian.

22. Eostaffella sp.
$L_3$5 (Appendix II),Matlock "Group",Brigantian.
Remarks: difficult to distinguish this genera in equatorial view ,but as very distinctive axial view.

23. Mikhailovella sp.
$L_3$1 (Appendix II),Matlock "Group",Brigantian.

24. Endothtranopsis sp.
$L_4$4 (Appendix II),Matlock "Group",Brigantian.
Remarks : spade-like later whorls.

25. Edothyranopsis cf. crassa (Brady 1876)
$L_3$4 (Appendix II),Matlock "Group",Brigantian.

26. Howchina cf. bradyana (Howchin 1888)
$L_6$2 (Appendix II),Matlock "Group",Brigantian.

27. Tetrataxis sp.
$L_4$2 (Appendix II),Matlock "Group",Brigantian.

28. Tetrataxis cf. conica (Ehrenberg 1854)
$L_4$3 (Appendix II),Matlock "Group",Brigantian.

29. Endothyra cf. kentuckyensis (Zeller 1953)
$L_4$7 (Appendix II),Matlock "Group",Brigantian.

30. Tetrataxis sp.
$L_4$3 (Appendix II),Matlock "Group",Brigantian.

31. Omphalotis cf minima (Rauser and Reitlinger 1936)
$L_3$5 (Appendix II),Matlock "Group",Brigantian.

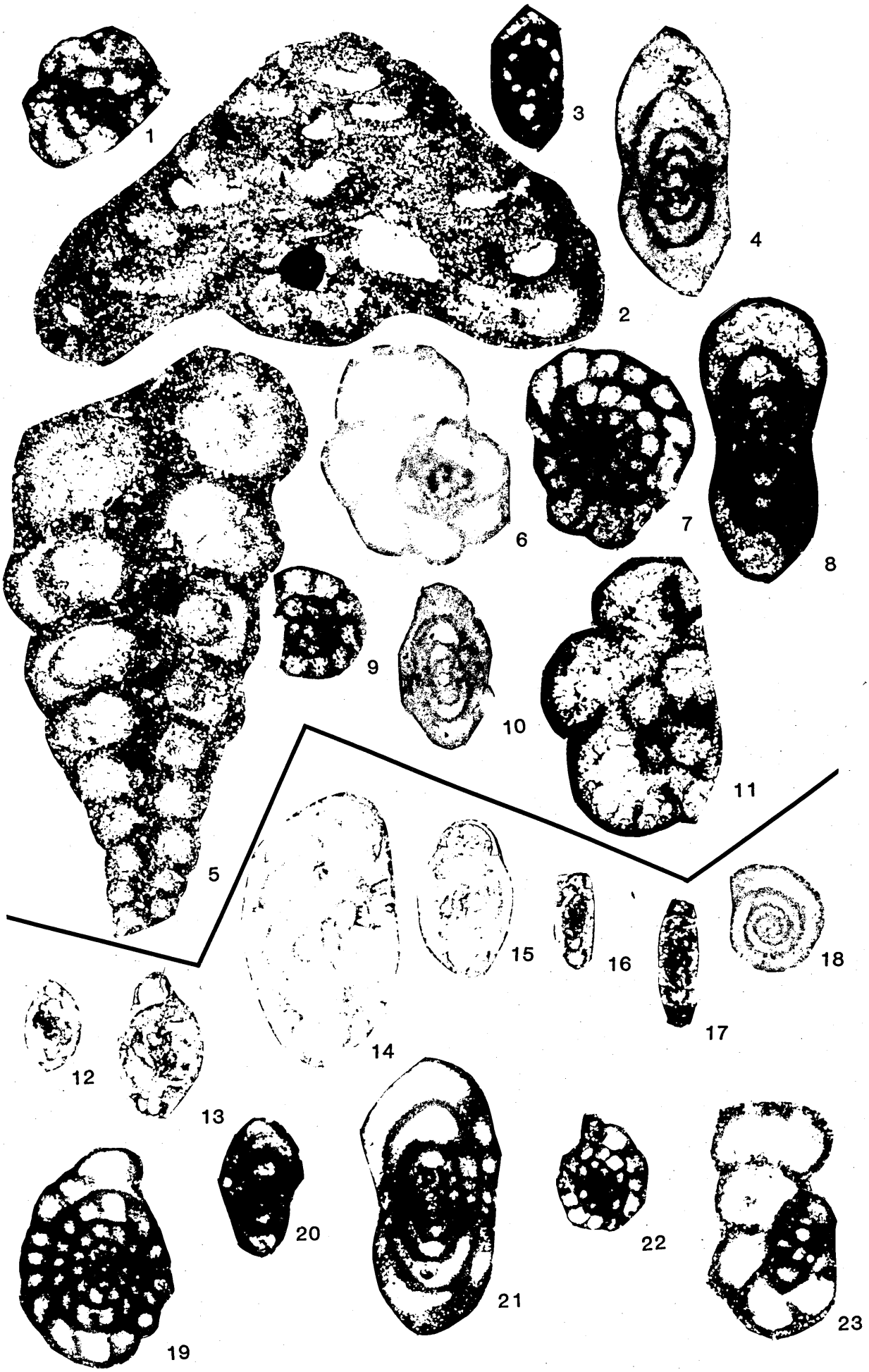
32. Endothyra sp.
$L_3$4 (Appendix II),Matlock "Group",Brigantian

33. Omphalotis cf. minima (Rauser and Reitlinger 1936)
$L_6$2 (Appendix II),Matlock "Group",Brigantian.

34. Koskinotextularia sp.
$L_4$3 (Appendix II),Matlock "Group",Brigantian
Remarks: lacking inner fibrous wall if present then resembles Palaeotextularia. The inner wall in this sample may possibly have been lost during diagenesis.

35. Eostaffella sp.
$L_2$3 (Appendix II),Matlock "Group",Brigantian.

PLATE 11



dolostones represent crinoidal-rich micarenites and sparenites. The incomplete dolomitisation appears to be due to the presence of sparry calcite, mainly crinoidal fragments, although cavity-fill cements and aggraded micrite may be important. The remnant calcite of the polyhedral pores became leached either during or after dolomitisation to give the variable primary dolostone porosities, ranging between 5 and 25 percent. These primary porosities became occluded during a later meteoric phase of diagenesis by large, anhedral, cavity-fill calcite.

Sub-aerial exposure and karstification during the Triassic, pre-Pleistocene and predominantly the post-Pleistocene has caused dedolomitisation and leaching to occur, and allowed a regeneration and enhancement of the primary dolostone porosity. Dedolomitisation and leaching have been found to be very localised, occurring mainly in association with solution-widened bedding, jointing and fracturing in the vadose zone, where an ample supply of aggressive water is available. This alteration of the dolostones can lead to porosities in excess of 40 percent. Away from the karst channels, dedolomitisation and leaching are limited and lower porosities develop. However, the presence of dolomite pseudomorphs (after crinoid ossicles), with their enhanced susceptibility towards dedolomitisation and leaching, gives rise to higher porosities here and in areas of excess leaching.

Dedolomitisation has been found occurring around the calcite-filled polyhedral pores and associated with the large micritised dolomite pseudomorphs. The localisation of the dedolomitisation around the calcite-filled pores, its enhancement near the surface beneath the soil horizon, and enhanced dedolomitisation of dolomite pseudomorphs at Harborough Rocks (a dolomite tor) are believed to be a consequence of vadose, rather than phreatic, waters. Phreatic waters would be more likely to cause a more pervasive dedolomitisation.

A geochemical study of the major elements (Mg, Ca, Fe, Mn, Si and Al) and trace elements (Na, K, Sr, Zn, Pb, Y and Br), including R.E.E. (Rare Earth Elements), of the limestones and dolostones was performed. The major elements were found to differentiate between micarenitic and sparenitic limestone due to the association of clay minerals and pyrite with the finer micritic material. The dolostones are non-ferroan, stoichiometric and enriched in most elements, apart from Sr, Si, Al and R.E.E.. The trace elements (mainly Na and Sr) and R.E.E. have shown that the dolomitising fluids did not have a similar origin to the mineralisation. However, these elements cannot clearly differentiate between the other modes of origin (such as hypersaline and groundwater) which have been suggested in the literature, particularly in the last twenty years.

ACKNOWLEDGEMENTS

I would like to thank the following:

1. Dr. Dennis Jackson, my supervisor, for obtaining an Open University grant and providing support and useful comments for three years.

2. The technical staff of the Open University Preparation Laboratory, in particular Andy Tindle, Dick Carlton, John Watson, Pete Webb and Andy Gledhill, for providing analytical facilities.

3. The staff of the Thin Section Room at the University, in particular Mr. Ian Chaplin, for his perseverance and help.

4. Moira Staerck and Jill Hewitt for the typing of the manuscript.

5. Jenny Wimpress-Hill and John Taylor for their helpful criticism in the preparation of the figures.

6. Dr. Barrett (Dresser Minerals Ltd.), Mr. Rauman (Steetley Minerals Ltd.) and Dave Bridge (I.G.S.) for their help in obtaining the borehole material and results.

7. Mr. John Williams (Aston University) for his perseverance and understanding during the drilling project in Derbyshire and following grievances.

8. Mavis Fewtrell for identifying the various foraminifera genera and her helpful comments upon the foraminifera section of this thesis.

9. Chris. Hawksworth for his help and constructive criticism of the Rare Earth section of this thesis.

10. The Open University for the award of a three-year research grant.

11. Colleagues and staff in the Department of Earth Sciences at the Open University for making my three years spent at the University very enjoyable.

DESCRIPTION

OF THE

TABLET.

I.

Crystallized Granular Limestone.

THIS Stratum which forms the surface from Langwith (where the river Poulter divides this County from Nottinghamshire) to Bolsover, where it bassets out, is composed of the following seven beds, subject to Faults as shewn in the Tablet.

No. 1. The top bed, of Isabella yellow colour, sparry texture, and small uneven fracture, being formed of minute rhombs in mass.

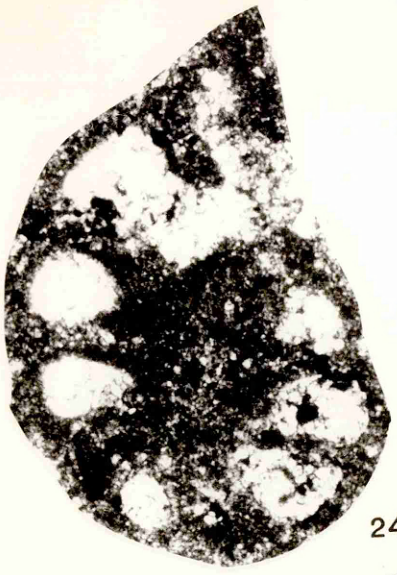
2. A variety, of straw yellow colour, much used for Building and makes neat Flooring, Staircases,

These beds make lime esteemed for Mortar, but not proper for Agriculture; the incumbent soil is not accounted productive of good herbage, but the luxuriancy of the Spiked Heath Brome-Grass is characteristic, and the sweet scented violet both blue and white, is very plentiful. Morels are very abundant in the month of April, at the roots of Ash and Elm trees, but not near the Oak; and the Mistletoe§ is found on the Crab, Thorn, Willow, Lime, Tacamahaca and Cherry trees; which it adorns with its parasitic foliage and crystalline berries, during the absence of the deciduous leaves in the winter months. Yellow rose trees with single and double, flowers grow luxuriantly in this soil, as may be noticed in gardens at Shireoaks near Whitwell; this soil, in some situations, as Hardwick, is very favourable to the growth of the Oak; in others, as Pleasley, it flourishes for a few years and then ceases; the Elm grows well, but the broad-leaved is subject to crack; the Walnut comes to a large size.

N. B. These beds are void of Petrifactions, but on breaking a block in Bolsover Field, in the Year 1795, of a ton and a half weight, a toad was discovered alive in the centre, which died immediately; no crack or joint was perceptible.....

White Watson(1811)

PLATE 12



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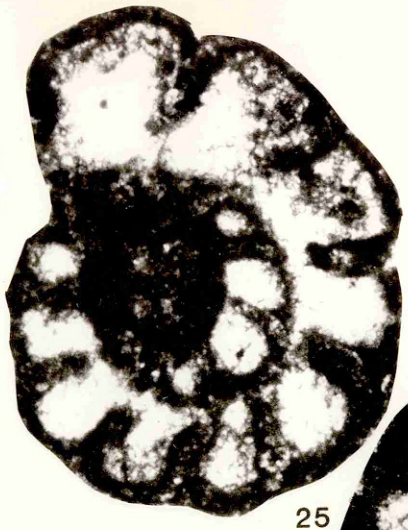

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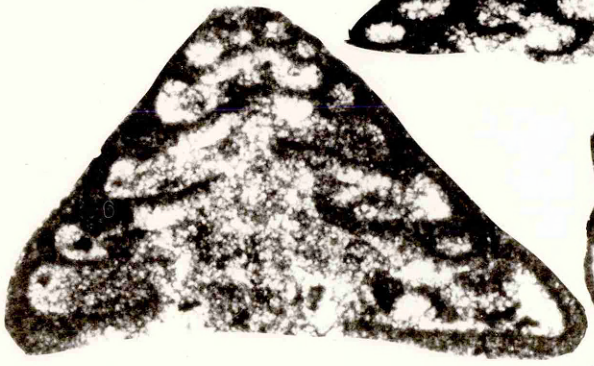

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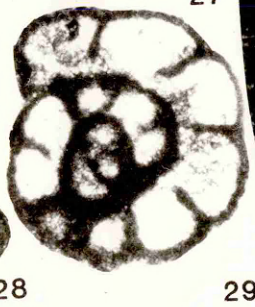

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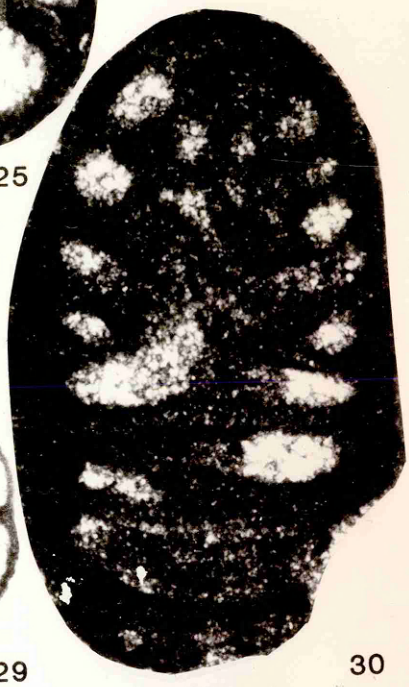

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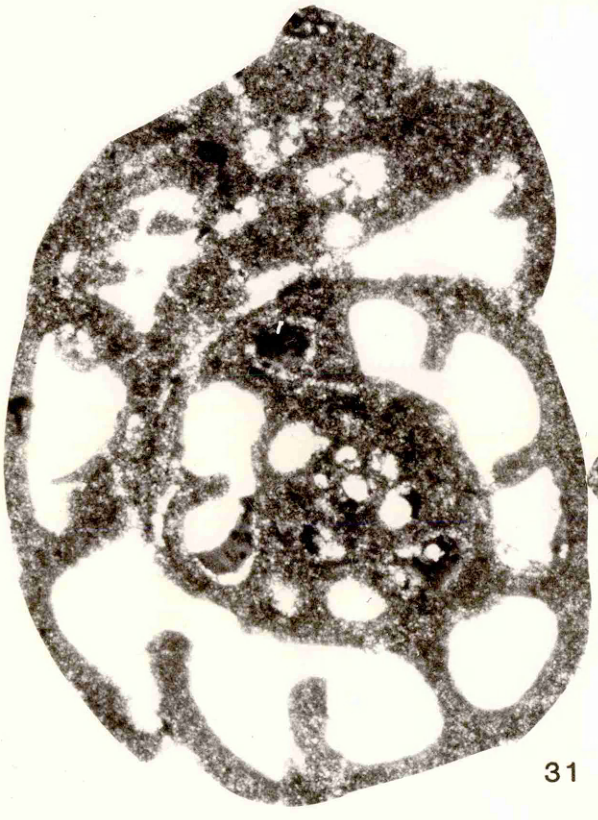

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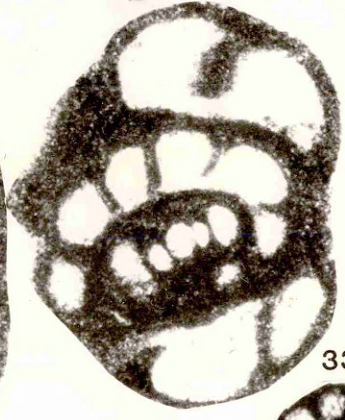

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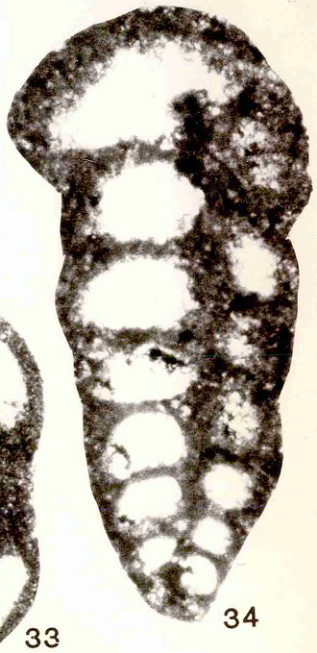

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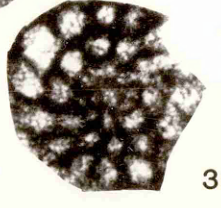

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Magnification for each plate x75

Plate 13 - Intake Quarry

1. Archaediscus cf. stilus (Grozdilova and Lebedeva 1954)
IQ 24 (Appendix II),Matlock "Group",Brigantian.

2. Archaediscus cf. convexus (Grozdilova and Lebedeva 1954)
IQ 16 (Appendix II),Matlock "Group",Brigantian.

3. Archaediscus sp.
IQ 11 (Appendix II),Matlock "Group",Brigantian.

4. Archaediscus cf. retidus (Conil and Lys 1964)
IQ 15 (Appendix II),Matlock "Group",Brigantian.

5. Archaediscus varsanofievae (Grozdilova and Lebedeva 1954)
IQ 4 (Appendix II),Matlock "Group",Brigantian.

6. Archaediscus cf. pseudomoelleri (Reitlinger 1854)
IQ4 (Appendix II),Matlock "Group",Brigantian.

7. Archaediscus cf. karreri (Brady 1873)
IQ16 (Appendix II),Matlock "Group",Brigantian.

8. Tetrataxis cf. conica (Ehrenberg 1854)
IQ 24 (Appendix II),Matlock "Group",Brigantian.

9. Eostaffella cf. mosquensis (Vissarionova 1948)
IQ 10 (Appendix II),Matlock "Group",Brigantian.

10. Pseudoammodiscus cf. nudus (Malakhova 1963)
IQ3 (Appendix II),Matlock "Group",Brigantian.

11. Earlandia sp.
IQ 3 (Appendix II),Matlock "Group",Brigantian.

12. Eostaffella sp.
IQ 4 (Appendix II),Matlock "Group",Brigantian.

13 Eostaffella sp.
IQ 17 (Appendix II),Matlock "Group",Brigantian.

14. Pseudoendothyra sp.
IQ15 (Appendix II),Matlock "Group",Brigantian.
Remarks: distinct 3-layered wall structure.

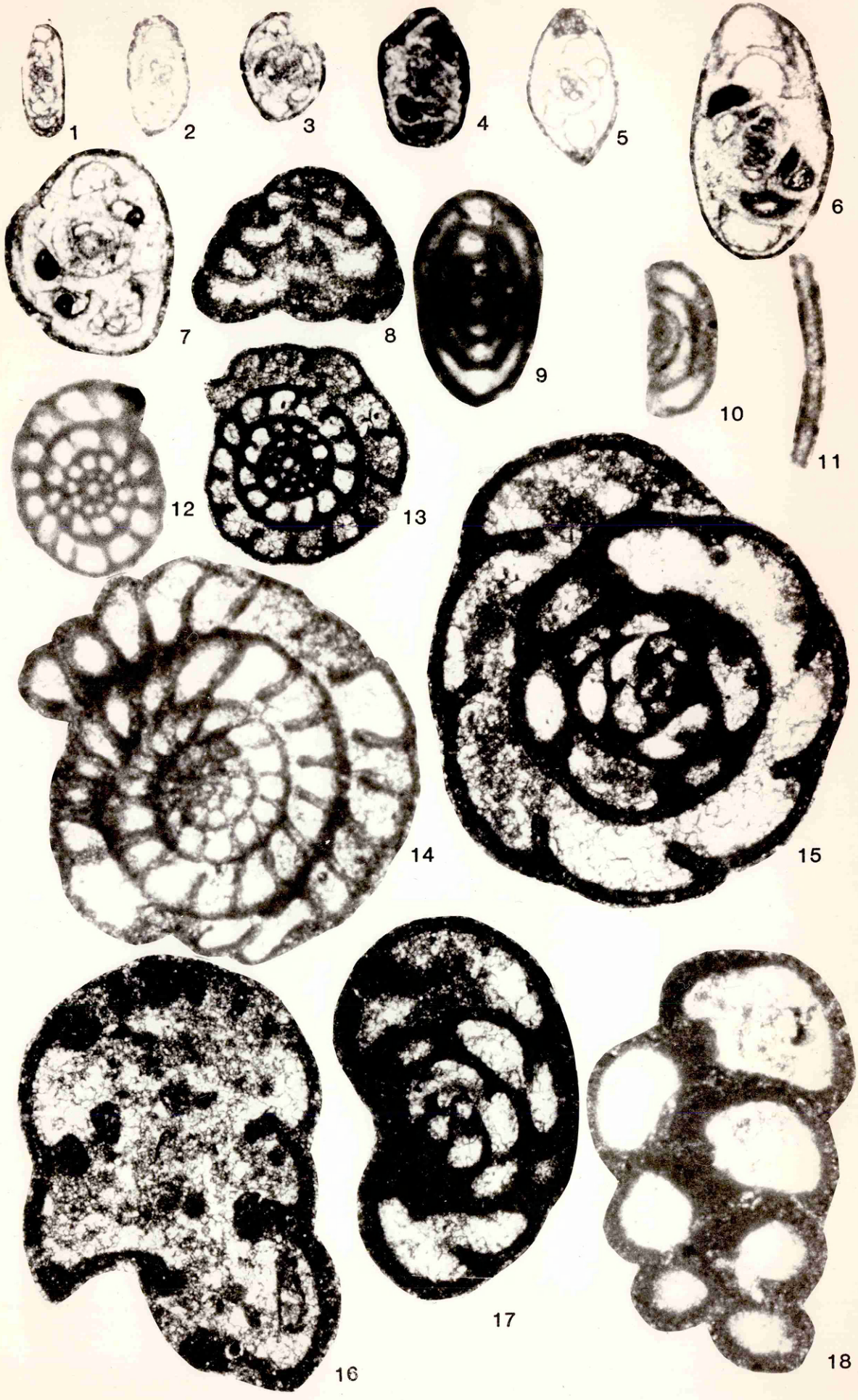
15. Globoendothyra sp.
IQ17 (Appendix II),Matlock "Group",Brigantian.
Remarks: very distinct wall structure - 3 layers, and short inclined septae.

16. Koskinotextularia sp.
IQ4 (Appendix II),Matlock "Group",Brigantian.
Remarks: presence of cribrae but lack of inner fibrous wall which may have been lost during diagenesis and thus could Cribostomum.

17. Globoendothyra sp.
IQ22(Appendix II),Matlock "Group",Brigantian.

18. Eotextularia sp.
IQ15 (Appendix II),Matlock "Group",Brigantian.
Remarks: very similar to Koskinotextularia,but has no inner fibrous wall though this may have been lost during diagenesis.

PLATE 13



The aim of the study was to see if the foraminifera could be used to define the Asbian - Brigantian boundary, and also to study the effect facies may exert upon the presence or absence of these genera.

The limestones of the Wirksworth area can be lithologically divided into two main groups (Section 2.1.); the lower unit called the Hoptonwood "Group" consists of pale massively-bedded limestones with an abundance of sparenites and crinoid fragments; and the upper Matlock "Group" which is more thinly bedded, has a dark colouration, and an abundance of micarenites with many brachiopod fragments. The much darker coloration of the Matlock Group has been shown to be due to the presence of organic matter. The groups are separated by a volcanic horizon, the Lower Matlock Lava. The uppermost Cawdor "Group", which is only sporadically developed, is found to lie unconformably on the Matlock "Group" and consists of thinly bedded chert-rich biomicarenites (Appendix I).

Following the classification of Vaughan (1905) for the Lower Carboniferous Limestone of the Bristol area zones, Sibly (1908) found the limestones to occur within the Dibunophyllum Zone (D) of the Dinantian. The Hoptonwood "Group" has a typical Dibunophyllum O (D_1) subzone fauna, the Matlock "Group" yields a typical fauna of the Lonsdalia floriformis subzone (D_2) and the Cawdor Group

has a typical fauna of the Cyathaxonia subzone (D_3). Extensive faunal lists for these limestones have been given by Sibly (1908), Wedd and Gibson (1913) and Smith et al. (1967).

George et al., (1976) erected six new stage names for divisions of the Dinantian in Britain. The Dibunophyllum (D) Zone of Vaughan is included within the Asbian and Brigantian Stages. The Asbian Stage included the Vaughanian Dibunophyllum O (D_1) subzone ie. the Hoptonwood "Group". The characteristic foraminifera are thought to be Archaediscus convexus and Howchinia sp.. The Brigantian Stage is approximately spanned by the Vaughanian D_2 and D_3 subzones and has a rich coral and brachiopod assemblage. The characteristic foraminifera are Neoarchaediscus sp., Asteroarchaediscus sp. and Bradyina sp..

Most of the foraminifera genera identified in these limestones can be shown to occur throughout the Asbian and Brigantian (Appendix II). Genera such as Howchinia, Koskinobigerina and Pseudoammodiscus are restricted to the Brigantian and likewise Forschiidae and Millerella are confined to the Asbian.

The absence of these index genera either in the Asbian or Brigantian in the Wirksworth rocks is not thought to be of any significance because, as both

Conil et al. (1980) and Fetwrell (pers. comm. 1980) have shown these genera to occur throughout the Asbian and Brigantian elsewhere in Britain.

Thus generic identification of the foraminifera in the Wirksworth rocks failed to yield genera that are diagnostic of either the Asbian or Brigantian Stages. This appears to be in direct contrast to the coral fauna which have been shown to change quite markedly at the Asbian/Brigantian boundary (Sibly 1908). Whether or not a change in foraminifera species at this boundary occurred, is beyond the scope of the art of foraminifera identification at the present time. Thus it becomes difficult to assess the effect which the facies change at the Asbian/Brigantian stage boundary had upon the foraminifera. Certainly no significant difference in foraminifera genera can be seen across the boundary.

It is felt that a facies change is the primary control upon the presence or absence of genera in these limestones (Appendix II). A lithological study of the limestones does indicate some correlation between the micarenites and the abundance of foraminifera genera (Appendix II). Certainly the great majority of foraminifera are found in the predominantly micarenitic Matlock "Group" and upper micarenitic part of the Hoptonwood "Group", whilst being relatively absent in the lower sparenitic

part of the Hoptonwood "Group". However, there are quite common examples of sparenites having an abundance of foraminifera genera and micarenites which have virtually no foraminifera present. The absence or presence of foraminifera in the sparenites may be related to sorting, ie. the foraminifera being absent from the coarser calcarenites due to their smaller size. Thus, from this study, it would appear that the lithology, as might be expected, is only one of a number of factors that may influence the distribution of these foraminifera.

The author accepts that the conclusions presented here must be taken with a great deal of caution as (a) only a limited number of samples were obtained and are not considered statistically representative of the total population (b) the use of Folk's classification is often misleading eg. sparenites may contain significant amounts of micritic material and (c) the identification of foraminifera in thin section is extremely difficult and commonly affected by diagenesis. Thus, the results are presented as a preliminary study of the foraminifera distribution in the Wirksworth area.

In conclusion, it appears that the foraminifera genera found in the limestones of this study do not differentiate between the Asbian and Brigantian Stages. It is felt that the presence and absence of particular foraminifera genera is a consequence of facies change.

CHAPTER FOUR

4. The Dolostones of the Wirksworth Area, Derbyshire: Their field relations, detailed petrography and diagenesis.

4.1 INTRODUCTION

The dolostones of the Wirksworth area form just one of a number of isolated dolostone outcrops in the southern part of the Derbyshire Dome. It extends some four kilometres east of the Brassington Fault, towards Wirksworth (fig. 5) and gives rise to a distinct topography with its tors and hillsides pitted with disused quarries and mine shafts. The dolostones weather to a typical yellowish-brown colour and have a very distinctive nodular appearance (pl. 14a). There is some variation in the weathering profile. Some beds in the Matlock "Group" (Section 2.2) appear more resistant than others and form prominent ledges due to the completeness of dolomitisation. That is to say, the more micritic limestones, so typical of the Matlock "Group", tend to become totally dolomitised by a volume for volume replacement. This develops little porosity and thus the beds are tight and tend to become more resistant to weathering. The network of small, sub-vertical, rib-like features (pl.14b) cutting across many weathered faces probably have a similar origin.

Apart from the abundant crinoidal fragments, macrofossils are rare, consisting of brachiopods, rugose and tabulate corals (especially Syringopora). Giganto-productids become more common in the Matlock "Group," where they occur in distinct bands and this is the major

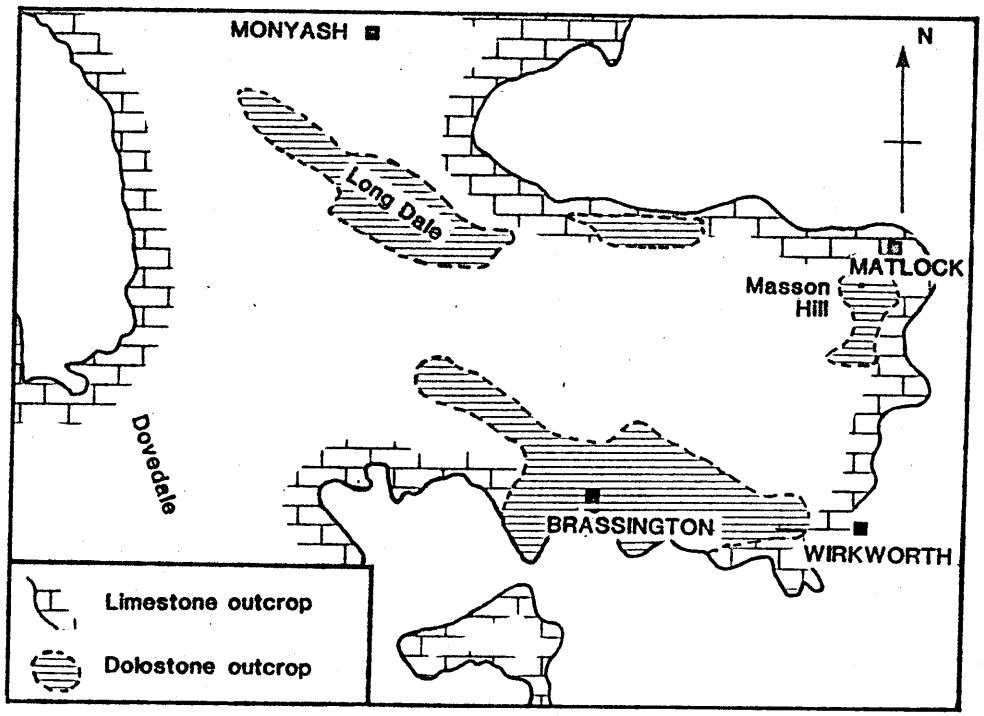
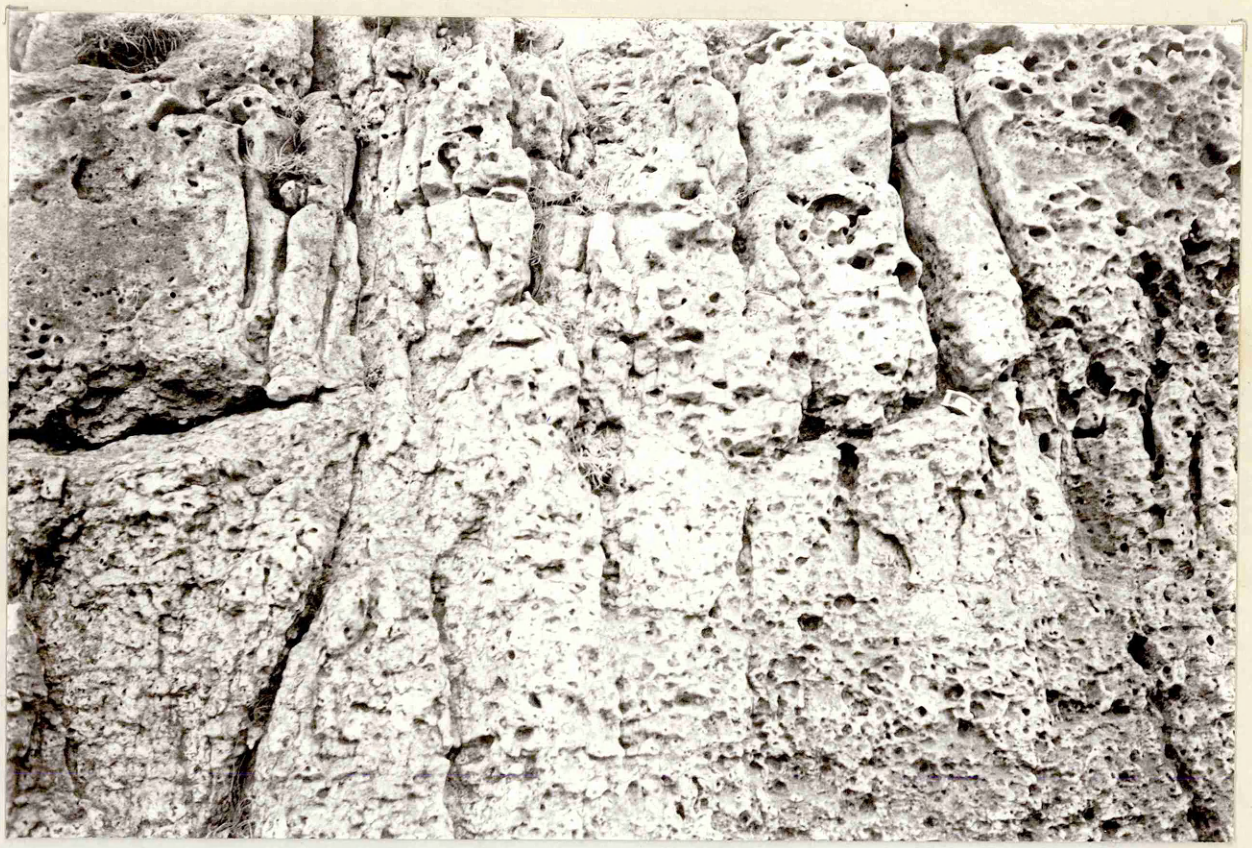


Figure 5 Map of the numerous isolated dolostone outcrops in the southern part of the Derbyshire Dome.



a

b

Plate 44 Weathering features of the dolostones in the Wirksworth area; (a) Typical cheesy weathering seen at Harborough Rocks and (b) rib of more resistant dolostone.

feature which characterises the group once it has become dolomitised. The most distinctive feature of the Hoptonwood "Group" is the abundance of crinoidal mouldic vugs, which gives the rock its characteristic cheesy appearance. Many mouldic vugs show remnant dolomitised syntaxial rims. These represent crinoidal fragments, some showing syntaxial rim development, which have become dolomitised (Section 4.4.1(2)) but have since been altered by dedolomitisation and leaching which have removed much of the dolomite pseudomorph to give the typical mouldic vugs.

The most detailed study of the petrography, field relations and geochemistry of the Wirksworth dolostones was that of Parsons (1922). Other contributions on various aspects of the area have also been made by Shirley (1959) and Smith et al. (1967), together with those working on the mineralisation (Dunham, 1952; Ford and King, 1965, 1966; King, 1966 and Ford 1967) and the silica pits (Hughes, 1952; Kent, 1957 and Walsh et al., 1972).

4.2 STRATIGRAPHY

A similar succession to that found in the surrounding limestone succession (Chapter II) can be identified within the dolostone outcrop. In ascending order this consists of dolomitised Hoptonwood and Matlock limestones: the Cawdor "Group" is not represented (fig. 1). The groups are recognised by (a) the Hoptonwood "Group" being relatively crinoidal rich,

and the Matlock "Group" relatively brachiopod-rich and (b) the Hoptonwood limestones are more massively bedded (1-2m.). The Lower Matlock Lava acts as a very useful stratigraphic marker. The lava does not crop out in the area, but does form a very prominent, easily-mapped feature. The presence of the lava has been proven by trial pits at Hopton Tunnel (ref. 266548) and Griffe Grange Quarry (ref. 256548), where the lava is weathered to a blue-green clay (section 2.1.).

The dolostone-limestone junction transgresses the stratigraphic boundary of the Hoptonwood and Matlock "Groups" (fig. 1), showing the dolomitisation to be clearly secondary. It is believed that dolomitisation occurred by seepage of dolomitising brines down joints (Dunham 1952). The origin of the brines is discussed in Chapter VII.

4.3 FIELD RELATIONS

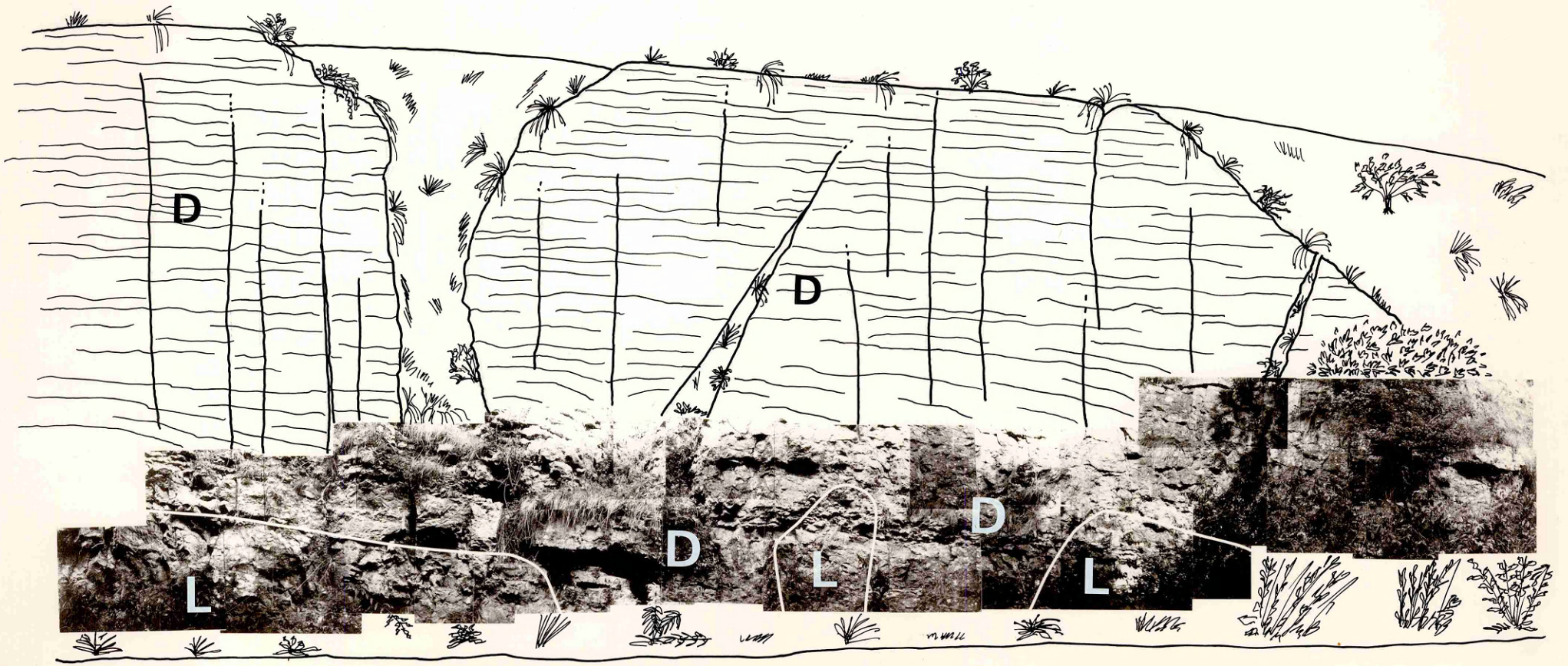
Parsons (1922) expressed a view that maximum dolomitisation occurred at Harborough Rocks and that it decreased away from that point. It can be shown from recent drilling that dolostone occurs to a depth of at least 50m. at Harborough Rocks (fig.36). However, recent drilling demonstrates that a greater thickness (150m.) of dolostones occurs at Ryder Point (ref. 261547) some 80m. below the height of the lowest topographical level seen at Harborough Rocks. Shirley (1959), Ford and King (1965, 1966) and King (1966) have described the undulatory nature of the base of the dolostones at Manystones Quarry (ref. 236552) (unfortunately now

infilled) and Golconda Mine (ref. 249552) fluctuating 40m. down prominent joints. This possibly explains the discrepancy between the ideas of Parsons, who believes that maximum depth of dolomitisation occurred at Harborough Rocks, and recent data which indicate even greater thicknesses occurring to the east, at Ryder Point. The control which joints exert on the base of dolostone can be seen in a number of places (fig. 13) (for example at Hopton Tunnel and near High Peak Quarry; Manystones and High Peak Quarries and the outcrop patterns above Hopton village; above Brassington village; near New Harborough Farm and just north of Pearsons Farm).

The Hopton Tunnel section occurs near the eastern edge of the dolostone outcrop within the Matlock Group. There the dolostone-limestone boundary can be seen to cut across bedding planes and rise and fall quite steeply, (pl. 15) suggestive of the dolomitisation occurring down vertical jointing. A section of the limestone remains undolomitised due to the protective nature of an overlying, slightly more argillaceous bed. However, adjacent to the undolomitised limestone the argillaceous matrix has been penetrated by the fluids and allowed dolomitisation to occur to lower depths.

The outcrops at Hopton village (ref. 258534), Brassington (ref. 231543), New Harborough Farm (ref. 246555) and Pearsons Farm (ref. 260557) show enclaves of limestone protruding sharply into the dolostone

Plate 15 Section along the High Peak Railway at Hopton Tunnel. Here the dolomitisation within the Matlock "Group" can be seen to rise and fall quite sharply, probably being controlled by former jointing

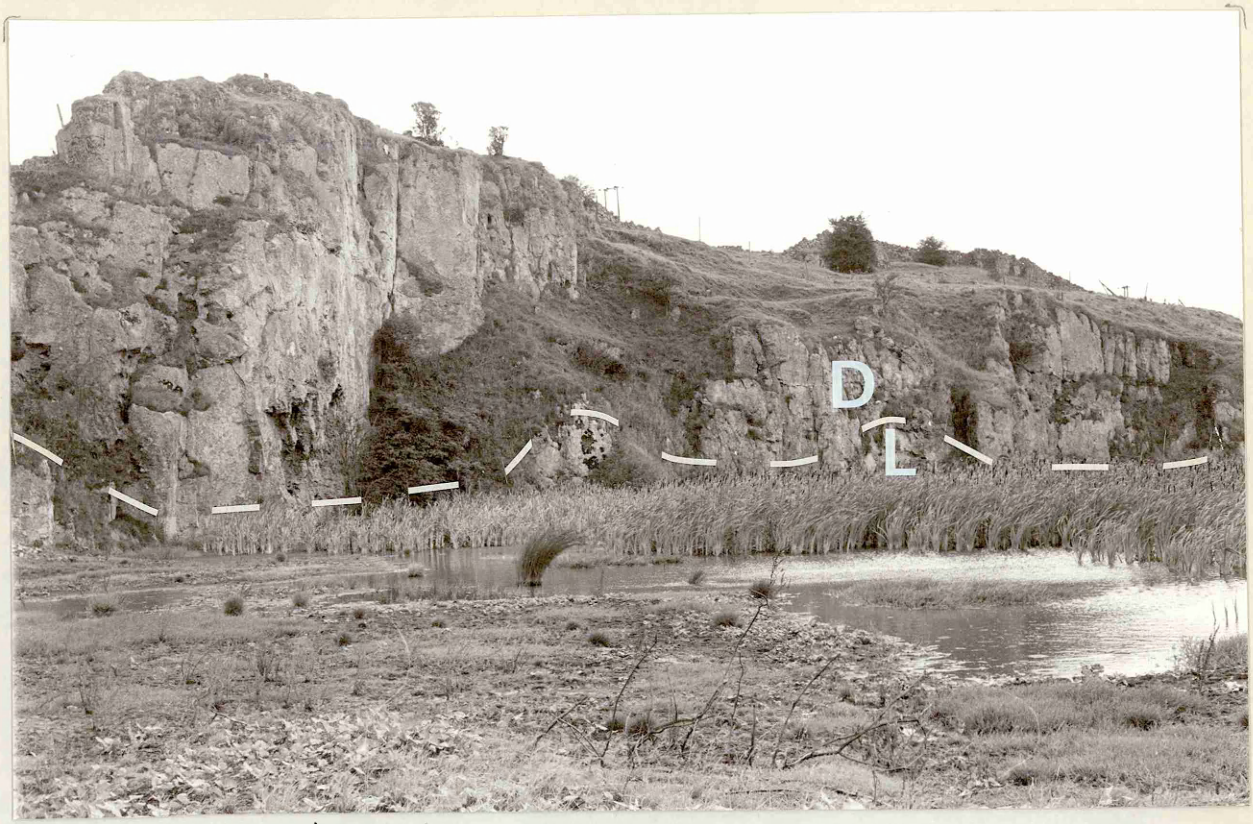


D = Dolostones

L = Limestones

outcrop (fig. 1). The enclaves are believed to be joint controlled due to their very sharp and vertical nature. The resistance to dolomitisation was probably a combination of dwindling dolomitising fluid supply and the limestone petrography, consisting of crinoidal biosparenites which tend to be more resistant to dolomitisation (Section 4.4.1(2)).

At Manystones and High Peak Quarries, and an adjacent railway cutting (ref. 235558), a sandwich of limestone occurs within the dolostone (pl. 16). The upper limestone-dolostone boundary is very irregular and dolostone penetrates the limestone sandwich down joints in a pendant-like manner (pl. 16). The extent of this penetration and distribution may reflect the resistance of the limestone to dolomitisation. The primary factor controlling the resistance of the limestone is its petrography. The limestone sandwich in this area consists essentially of a crinoidal biosparenite, which tends to be quite resistant towards dolomitisation (Section 4.4.1(2)). The variations that may occur in individual limestone beds, such as the presence of more easily dolomitised micritic material, may explain the irregular upper surface and the lateral discontinuity. The lower surface is planar (pl. 16), due to the presence of a thin clay wayboard, which prevents dolomitisation from below. In each of these outcrops the irregular upper surface has been karstified and subsequently infilled by a phase of lead-zinc mineralisation. This is the



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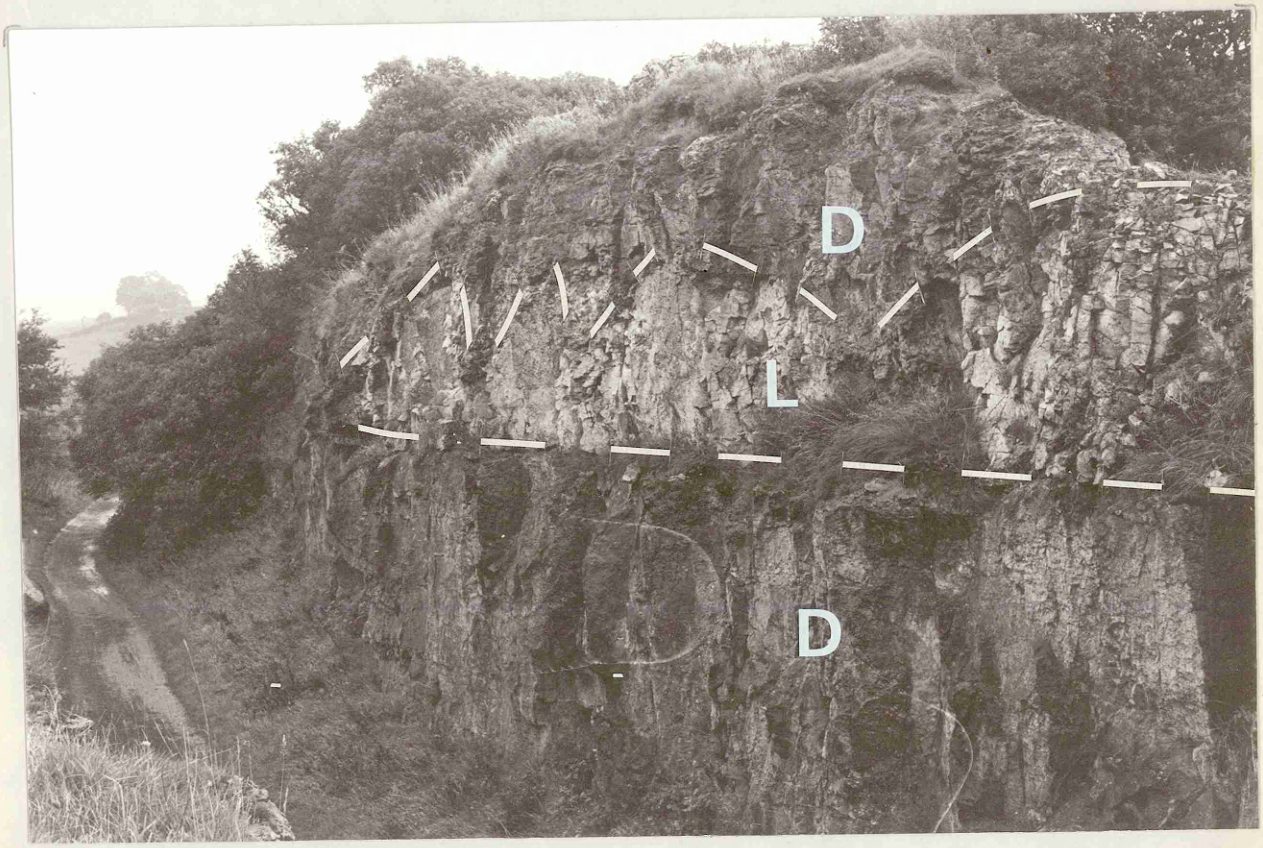


b

Plate 16 "Sandwich" of limestone within the dolomitised Hoptonwood "Group", occurring throughout the eastern part of the study area (a) at Manystones Quarry, showing the irregular upper surface and (b) at a cutting near High Peak Quarry, showing the irregular upper surface plus the planar lower surface.

typical mode of the mineralisation in this area (Section 6.2). Small outcrops of limestone in quarries opposite Curzon Lodge (ref. 233557) also show vertical dolostone bodies penetrating probably down joints into unaltered limestone. The boundary is marked by a coarsely-crystalline calcite vein probably associated with the widespread lead-zinc mineralisation.

Other examples of limestone enclaves within the dolostone outcrop occur just to the east of Tiremare Lane (ref. 264539) below the inferred position of the Lower Matlock Lava which forms a prominent feature along the hillside. It is believed that these areas of limestone have remained undolomitised due to the protective nature of the overlying lava, from downward seeping brines.

Dolomitisation can thus be shown to be joint-controlled and the origin of the fluids was from above, although bedding solution channels and stylolites, formed during diagenesis in late Lower Carboniferous times, must have played a significant role. According to Parsons (1922) the faults seen in the area (fig.5) appear to be post-dolomitisation as they can be shown not to influence the pattern of dolomitisation. It is believed by most writers (Dunham 1952, Kent 1957, Ford 1967) that the dolomitising fluids seeped downwards from the overlying Zechstein Sea. However King has suggested that the dolomitisation could be an early phase of epi-syngenetic mineralisation (Ford 1968). The possible

origins of the dolomitising fluids is fully discussed in Chapter VII.

4.4 DETAILED PETROGRAPHY

In detail the dolostones of the area exhibit a variety of fabrics and textures. The more important of these, from the point of view of controlling the development of porosity in the dolostones, are crystal size and shape. Individual beds, although primarily consisting of a particular crystal size and shape, will show a great deal of variation, giving poikilotopic and porphyrotopic textures (Friedman 1965). The variation can be shown to be controlled by the fabric of the replaced limestone. The great variation of limestone types (Appendix 1) produces a great variety of dolostone textures in the Wirksworth area. Each type of dolostone will have its own particular type of porosity (Chapter V). Each dolostone type shows a number of characteristics including; fossils, zoning, pore-filling calcite and dedolomitisation, and these will be dealt with in the following discussion.

4.4.1. DOLOSTONE TYPES

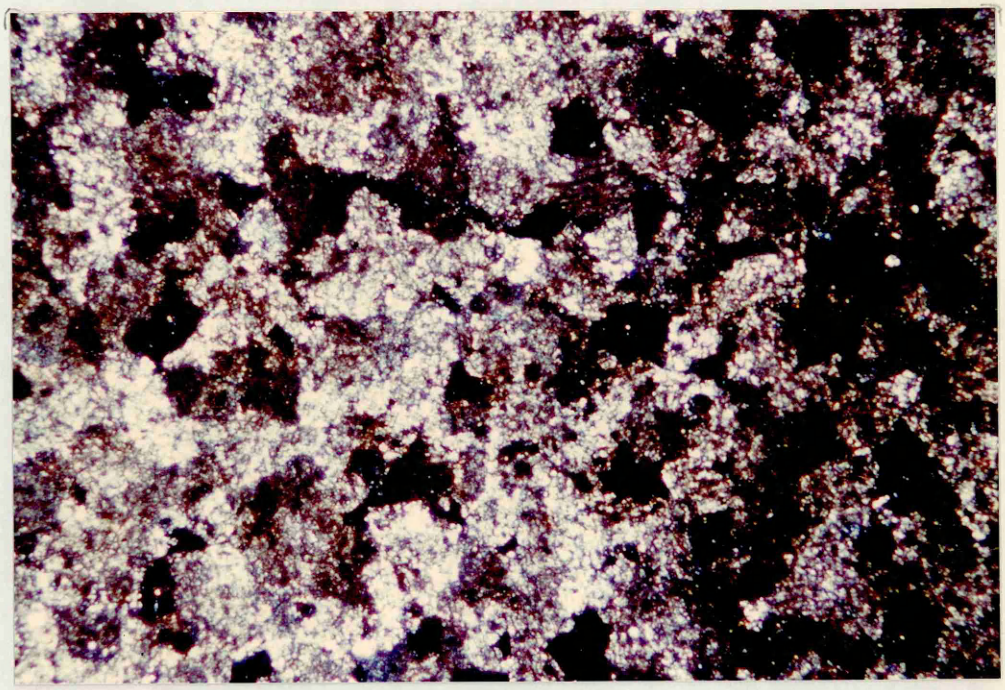
The classification used here for the dolostones follows Friedman (1965). Three categories are recognised, comprising (1) Xenotopic (poor crystal shape); (2) Hypidiotopic (poor-good crystal shape) and (3) idiotopic (good crystal shape). Within each of these categories crystal size will vary and this is discussed.

As stated, a mixture of crystal shapes can be present within a single bed, although there is usually a dominant crystal shape, upon which the dolostones are classified. This gives four basic dolostone types: (1) completely dolomitised xenotopic dolostone; (2) incompletely dolomitised xenotopic-hypidiotopic dolostone; (3) idiotopic dolostone and (4) dolomitic limestone.

For the purpose of this study it is assumed, in accordance with Murray (1960), that a volume for volume replacement of the former limestone has taken place (Section 5.2). Certainly, when considering the completely dolomitised xenotopic dolostones, a volume for volume replacement is suggested by the very low porosity (av. 3%), in that a molecule for molecule replacement would be expected to give at least 12-13% porosity, if we consider no porosity existed in the original limestone. The other dolostone types, the incompletely dolomitised xenotopic-hypidiotopic and idiotopic dolostones are believed to be replaced in a similar manner. The greater porosities of these dolostones are thought to be a consequence of incomplete dolomitisation and leaching, rather than a molecule for molecule replacement.

(1) Completely Dolomitised Xenotopic Dolostone

These dolostones consist of a tightly-interlocking mosaic of poorly developed crystals of dolomite which have porosity ranging from 4-8% and showing few if any good crystal faces (pl.17a). The crystal size of these



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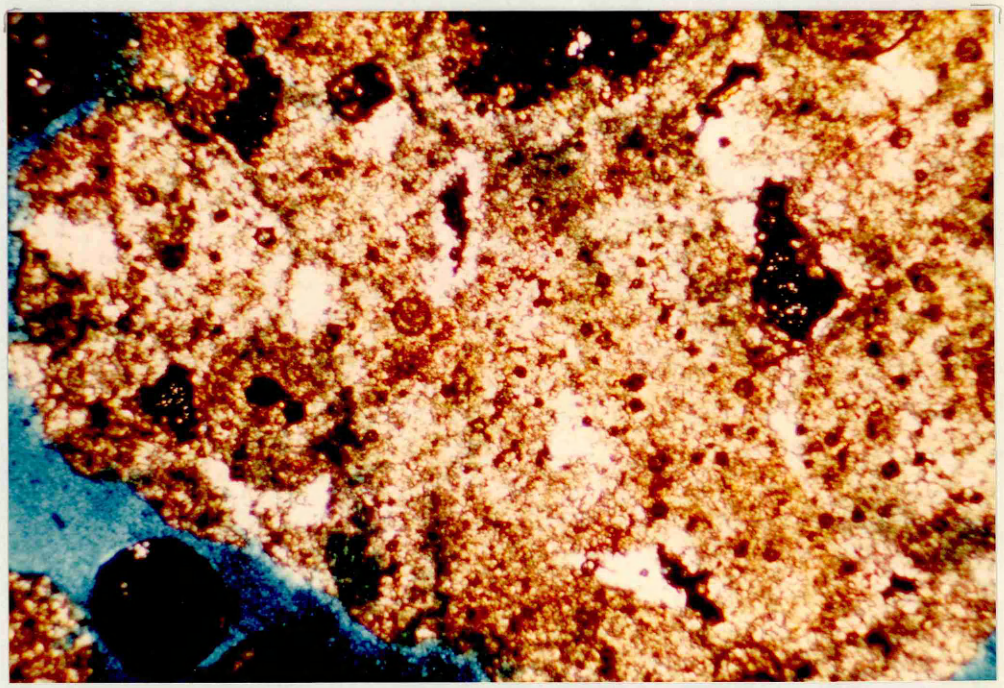


b

Plate 17 Dolostone types;(a) completely dolomitised xenotopic dolostone showing poor crystal forms and no calcite-filled pores, and (b) a more finely crystalline xenotopic dolostone,showing remnant textures. x80

dolostones can be seen to vary considerably giving two major types, microcrystalline (5-20um) and mesocrystalline (50-200um) xenotopic dolostones. The much finer dolomite tends to mimic the former limestone fabrics, due to the crystal size. Similar mimicry has also been noted by Chilingar (1956) and Schmidt (1965). Many of the finer details of the former limestone, such as foraminifera and microspar produced by neomorphic aggradation can be identified even after complete dolomitisation. In the micrite matrix much larger fossil fragments such as crinoidal fragments, which tend to be pseudomorphed by large anhedral dolomite crystals (often showing syntaxial rims), give a very pronounced porphyritic texture. It is rare to find undolomitised crinoidal fragments (marked by a calcite-filled or mouldic pore) in these finer dolostones, when compared to the much coarser dolomite. This is indicated by the incompletely dolomitised xenotopic-hypidiotopic dolostones. This probably reflects the greater supply and access of fluids to the finer dolostones, allowing dolomitisation of even the more resistant fragments, such as crinoids. The much coarser dolomite tends to obliterate the much finer fossil material and thus only the much coarser fossil material remains identifiable, such as crinoidal and brachiopod fragments.

The coarser dolomite crystals appear cloudy due to the number of inclusions. These consist of insoluble material, such as clays and ferric compounds, and possibly

remnant calcite from the former limestone. Similar inclusions have been described by Evamy (1967) in the dolostones of the Jura. These inclusions probably occur in the much finer dolostones but these are less obvious because of the smaller crystal size. In some samples the inclusions outline features of the former limestone fabric, indicating areas of sparry calcite (cleaner dolomite) and allochems (usually giving cloudy dolomite). Murray and Lucia (1967) recorded similar textures to those found in the Wirksworth dolostone, the inclusions outlining a former grainstone texture, but as with the dolostones of this study, found this to occur only rarely. Bishop (1968) suggested that such textures represent replacement of sparry calcite giving a clean dolomite, and micrite giving a cloudy dolomite, as both micrite and clay material tend to have similar environments of deposition. The much coarser xenotopic dolostones (500μ) are possibly due to the replacement of a crinoidal calcarenite, the crystals representing numerous pseudomorphs after crinoidal fragments, and are similar to the dolostones described by Armstrong (1970) in the Brooks Range, Alaska. These are rare due to the fact that crinoidal limestones are relatively resistant to dolomitisation.

Microcrystalline xenotopic dolostones in modern sediments have been shown to be primary or penecontemporaneous. That is to say, forming within

the marine environment, involving hypersaline brines causing the formation either as primary precipitates (Von der Bosch and Jones 1976) or the alteration of recently deposited carbonate muds by magnesium-rich brines. Many examples of primary fine-grained dolomite have been identified in modern environments, associated with hypersaline brines, by Shinn et al. (1965) in the Bahamas, Alderman and Skinner (1957) and Von der Bosch (1965) in the Coorong, S.E. Australia, Clayton et al. (1968), Deep Springs Lake, California, Deffreyes et al. (1965) at Bonaire, Lesser Antilles and Illing et al. (1965) in the Persian Gulf. No evidence of a former hypersaline environment, such as evaporites, restricted fauna, intraformational breccia (which represents removal of evaporites by solution and subsequent collapse of the surrounding dolostone), or length-slow chalcedony (which tends to replace evaporite minerals such as gypsum), can be found in these dolostones.

The microcrystalline dolostones of this study (pl. 17b) are believed to be secondary, having an identical origin to the mesocrystalline dolostone. The presence of the dolomitised crinoid and brachiopod fragments indicate the secondary nature of the dolomitisation, and the normal marine nature of the fauna indicate no primary influence of hypersaline brines. The chemistry of both types of dolostones shows no

significant difference and both the finer and coarser dolostones are believed to be formed from the same late diagenetic dolomitising phase. The prime control upon crystal size appears to be the physico-chemical conditions existing within the primary limestones.

Sample No.	Crystal Size(u)	CaO %	MgO %	CaO/MgO	Fe_2O_3 %	Mn^{++}	Sr^{++} p.p.m.	Pb^{++}	Zn^{++}
67-70	50-100	30.90	20.88	1.48	0.33	1009	80	6.0	49.8
136-139	50-100	30.71	21.46	1.43	0.30	----	--	---	----
103-106	100-150	30.16	20.60	1.46	0.29	873	69	6.0	35.9
36-39	200-300	30.20	21.54	1.40	0.32	854	51	62.1	65.8
118.121	200-300	34.53	18.08	1.91	0.33	1039	77	14.5	40.8
130-133	300	30.80	21.28	1.45	0.28	1096	57	20.9	16.7

It would appear from the foregoing, and the evidence from the partially dolomitised limestones around the dolostone outcrop, that the xenotopic dolostones represent a dolomitised micrite. The completeness of dolomitisation is thought to be caused by the greater susceptibility of the micrites towards dolomitisation, often becoming dolomitised first, as noted by Thomas (1962), Schmidt (1965) and Murray and Lucia (1967). The variation of the crystal size is due to the spacing of dolomite nuclei (Chilingar, 1956), i.e. closely-packed nuclei would produce a finely-crystalline xenotopic dolostone. The different nucleation densities of dolostones will depend upon a number of factors, such as permeability, particle size, mineralogy, clay material and possibly organic matter, of the original limestone. The variation in any of these factors may lead to the differing density of the dolomite nuclei, thus giving rise to a variable crystal size.

Permeability

The permeability controls the volume of fluid allowed to penetrate a particular rock, and is probably the single most important factor influencing the extent of dolomitisation. A relatively high permeability would allow the nucleation of many crystals of dolomite and give rise to a finely-crystalline dolostone, whereas a lower permeability would allow only isolated nuclei and a coarser dolostone would develop.

Nicholls (1974) gives a good example of permeability control upon crystal size in the dolostones of Panther County, Nevada. Here a supratidal, finely-crystalline dolostone is underlain by coarser diagenetic limestones. The dolomite formed from downward seeping hypersaline brines from the overlying supratidal environment. The fine-grained dolostone is due to the alteration of the very permeable, uncemented lime mud on the sea floor, whereas the permeability of the underlying carbonate was much lower due to the diagenesis, and thus allows a coarser dolostone to develop.

Particle Size

Particle size will control the amount of surface area available for chemical attack. An increase in particle size will cause a decrease in the surface area of the crystal and porosity, and allow fewer crystals to nucleate. Folk (1965) has shown that

aggradation of the micrite can occur during neomorphism to give a coarser microspar and can be shown to have occurred in many of the stratigraphically equivalent limestones (Section 3.1.2). This increase in crystal size, within the matrix, is believed to be a major control upon the crystal size in these dolostones. It may explain to a certain degree the abundance of meso-crystalline dolostones, rather than cryptocrystalline dolostones, in view of the many micrites occurring in the succession (Appendix I).

Mineralogy

Prior to the diagenesis of the former limestone and consequential stabilisation of the various carbonate phases, the original lime mud would be composed of a variety of minerals but principally of aragonite and high-magnesium calcite. The susceptibility of these minerals towards dolomitisation has been noted by Schmidt (1965) in the Gigas beds of Germany; however, the former limestones are believed to have been stabilised to the low-magnesium calcite (Table IV), prior to dolomitisation (Section 3.3). The stabilisation of the high-magnesium calcite has recently been discussed by Davies (1977) and Meyers and Lohmann (1978). Davies has found that a higher magnesium content (1.5%) will remain in calcite after stabilisation. Meyers and Lohmann (1977) indicate that upon recrystallisation of high-magnesium calcite, such as crinoidal fragments, the magnesium is not lost

but forms localised microdolomitic inclusions. However, these inclusions have only been noted in crinoidal fragments, primary fibrous cements and syntaxial rims. On the other hand the presence of high-magnesium calcite in lime muds must allow the possibility of their presence within micrites. These microdolomitic inclusions may provide ideal nuclei for dolomite growth, although in these limestones the geochemistry suggests that the lime muds were primarily aragonitic. Lindholm (1969) recognised fine detrital dolomite (originating in supratidal areas) being present within lime mud and acting as nuclei for dolomitisation.

Clay Minerals

Clay minerals will tend to be associated with the finer carbonate material, due to the similar environments of deposition. The presence of these clay minerals may influence considerably the micrites susceptibility towards dolomitisation. Kahle (1965) and Schmidt (1965) have directly attributed the degree of dolomitisation to the amount of clay minerals present in the former limestone. These authors believe the clay minerals act either as catalysts or nuclei for reaction. However Zenger (1965), Hatfield and Rohrbacker (1967) and Lumsden (1973) can find no such correlation between clay and dolomite. If dolomitisation is dependent upon the insoluble residue content, then

an increase of this residue should increase the degree of dolomitisation and decrease the crystal size by increasing the density of nucleation centres. Table V shows no such correlation between the degree of dolomitisation (indicated by the $CaCO_3$) or crystal size with the insoluble residue content of the dolostones in the Wirksworth area. Although not directly attributing to the dolomitisation, the clay mineralogy may have some influence upon the nucleation of the dolostones, in that magnesium-rich clays such as chlorite and montmorillonite may act as insoluble nuclei.

In addition a few authors (Schmidt, 1965, Al-Hashimi, 1971) have considered the association of organic matter with the micritic material. Certainly the finely-crystalline material of the Matlock Group has quite a marked organic content, giving the group its dark colouration. The decomposition of this organic matter may set up favourable Eh and pH conditions for dolomitisation to occur.

In conclusion, crystal size in the dolostones is primarily controlled by the distribution of its nuclei. This distribution could be influenced by many of the factors mentioned above, and so many crystal sizes should develop, considering the variable fabric of the former limestone. The greater permeability, smaller particle size, favourable mineralogy, and

	$CaCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$	Total
Micrite	97.71	1.10	0.00	0.000	98.81
Micrite	98.69	0.50	0.00	0.00	99.19
Micrite	98.17	0.63	0.00	0.00	98.80
Neom. Aggradation	98.20	0.21	0.00	0.08	98.57
Neom. Aggradation	98.30	0.36	0.00	0.00	98.66
Neom. Aggradation	97.86	0.67	0.00	0.00	98.53
Primary Cement	96.66	0.92	0.07	0.15	97.80
Primary Cement	96.43	0.74	0.02	0.00	97.19
Cavity Fill Cement	98.53	0.93	0.00	0.00	99.46
Cavity Fill Cement	98.34	0.00	0.00	0.00	98.34
Cavity Fill Cement	98.03	0.74	0.02	0.10	98.89
Cement Synt. Rims	99.29	0.16	0.00	0.09	99.64
Cement Synt. Rims	99.35	0.76	0.00	0.00	100.01
Cement Synt. Rims	99.81	0.28	0.00	0.08	100.17
Neom. Synt. Rims	97.96	0.19	0.09	0.00	98.24
Neom. Synt. Rims	99.28	0.00	0.22	0.00	99.50
Neom. Synt. Rims	98.34	0.41	0.00	0.00	98.75
Crinoid Fragments	96.53	1.03	0.00	0.21	97.75
Crinoid Fragments	98.21	1.11	0.00	0.10	99.42
Crinoid Fragments	98.75	0.55	0.00	0.00	99.30
Crinoid Fragments	98.69	0.42	0.00	0.00	99.11
Brachiopod Fragments	98.92	0.00	0.21	0.00	99.13
Brachiopod Fragments	98.41	0.72	0.09	0.05	99.27
Brachiopod Fragments	98.20	0.64	0.00	0.00	98.84
Foraminifera	95.04	0.12	0.00	0.18	95.31*
Foraminifera	94.90	0.20	0.00	0.08	95.18*
Algae	100.15	0.00	0.00	0.00	100.15
Algae	97.89	0.25	0.28	0.00	98.40

Neom.=Neomorphic *poorly polished sample

Synt.= Syntaxial Rim

Table IV The probe analyses of the various minerals constituting the numerous textures and fabrics found in the limestones. Samples $L_1$6m Mid. Pk. Qu. and IQ 16 It. Qu.

Sample No.	Insol. Res(%)	CaO/MgO(wt.%)	Porosity(%)	Crystal Size(u)
36-39m.	2.177	1.410(X)	22.4(M)	200-300
67-70m.	0.319	1.500(X)	20.3(M)	50-150
70-73m.	0.491	1.480(H)	17.6	100-150
88-91m.	0.387	1.460(H)	10.8	100-200
103-106m.	0.606	1.480(H)	13.8	100-150
118-121m.	0.315	1.900(H&D)	19.0	200-300
130-133m.	0.312	1.520(H)	11.0	300
136-139m.	0.638	1.410(H)	12.5	50-100
148-151m.	0.502	1.520(H)	13.0	200
Typical Limestones				
L_2 7	5.655	Br.Biosparenite-Hoptonwood 'Group'		
L_6 6	1.975	Cr.-Br.Pelsparenite-Matlock 'Group'		
HW26	0.838	Br.Biomicarenite-Matlock 'Group'		

M=Mouldic Pores X=Xenotopic Dolostone H=Hypidiotopic Dolostone
D=Dedolomitisation

Table V A comparison of the various dolomite crystal sizes with the corresponding insoluble residues, indicating that there is no relation between these components.

	$CaCO_3$	$MgCO_3$	$FeCO_3$	$MnCO_3$	Tot.	$mCaCO_3/MgCO_3$
Dolomite	53.45	43.45	0.41	0.00	97.31	1.03
Dolomite	54.49	44.83	0.29	0.20	99.81	1.02
Dolomite	54.88	45.16	0.07	0.00	100.11	1.02
Dolomite	53.43	44.87	0.14	0.08	98.52	1.00
Dolomite	58.86	40.77	0.00	0.00	99.62	1.21
Dolomite	58.62	40.14	0.14	0.00	98.90	1.23
Dolomite	58.04	41.62	0.00	0.00	99.66	1.17
Outer Zone	55.12	43.40	0.14	0.00	98.66	1.07
Outer Zone	53.84	44.38	0.00	0.00	98.22	1.02
Cavity Fill Cement	98.73	0.72	0.08	0.00	99.53	
Cavity Fill Cement	97.76	0.04	0.00	0.00	98.09	
Cavity Fill Cement	99.53	0.34	0.10	0.19	99.87	
Dedolomitisation	91.24	8.14	1.27	0.00	100.65	
Dedolomitisation	90.95	7.77	0.23	0.00	98.95	
Dedolomitisation	96.60	4.19	0.00	0.00	100.79	
Ded^n of Pseudomorphs(C)	96.26	1.62	0.00	0.00	96.88	
Ded^n of Pseudomorphs(C)	96.39	1.94	0.02	0.00	98.35	
Ded^n of Pseudomorphs(C)	100.90	1.16	0.00	0.00	102.06	
Ded^n of Pseudomorphs(E)	93.05	5.98	0.00	0.00	99.03	
Ded^n of Pseudomorphs(E)	90.90	8.33	0.00	0.00	98.53	

Ded^n= Dedolomitisation C= centre of crystal
E= edge of crystal

Table VI The probe analyses of dolomite constituting the various fabrics and textures found in the dolostones. Samples from Griffe Grange Qu.

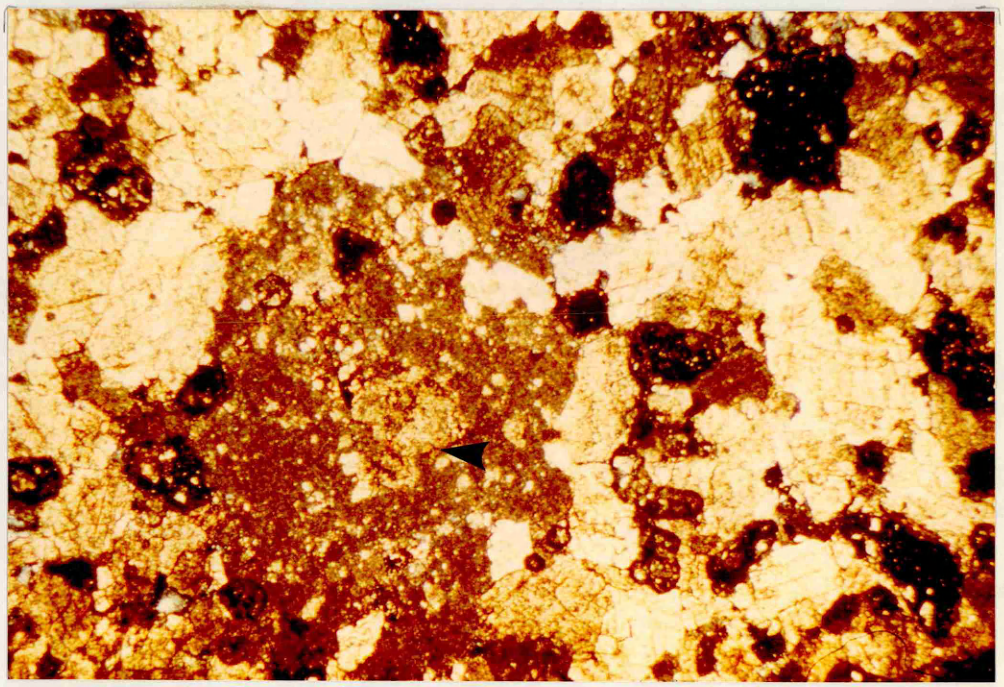
presence of clay and organic material may go some way to explain the greater susceptibility of micritic material during dolomitisation when ,compared to the more coarsely-crystalline sparry material.

The xenotopic dolostones probably represent dolomitised micarenites and biomicarenites (fig. 6). Any fossil material is invariably dolomitised due to the access of dolomitising fluids, allowing complete dolomitisation of even the more resistant fragments such as crinoids. The xentopic dolostones can be found in the Hoptonwood and Matlock Groups, however appear to occur predominantly in the Matlock "Group" due to the presence of numerous micarenites.

(2) Incompletely Dolomitised Xenotopic-Hypidiotopic Dolostone

These dolostones are very similar to those described in the previous section, showing all the variation of crystal size and textures. However, included within the interlocking mosaic of anhedral dolomite, are scattered polyhedral pores (pl.18a), many of which have become filled by calcite. These represent an intermediary between the low-porosity xenotopic dolostones and the high-porosity idiotopic dolostones, although much of the porosity has now been occluded by a cavity fill cement.

a



b

Plate 18 Colour photomicrographs;(a) incompletely dolomitised hypidiotopic dolostone showing the development of calcite(pink) filled pores and (b) dolomite pseudomorph after a crinoidal fragment,showing enclosed euhedra.Harborough Rocks. x80

The polyhedral pores are believed to be formed by the incomplete dolomitisation of large crystals of calcite, which are thought to have a mainly crinoidal origin due to the abundance of these fragments in the stratigraphically equivalent limestones, which were probably crinoidal biomicarenites (fig. 6). Murray (1960), Goldberg (1967) and Murray and Lucia (1967) all give examples of this type of selective dolomitisation which alters micrite but leaves crinoidal fragments undolomitised. At a later stage, these crinoidal plates may either become leached to give mouldic vugs or dolomitised to give large anhedral pseudomorphs (pl. 18b). In the dolomites of this study both leaching (mouldic vugs now filled with typical cavity-fill cement) and dolomitisation can be shown to have occurred, often within the same sample. Thus some fundamental factor appears to influence the susceptibility of these fragments during dolomitisation. This may be a physical factor of the fragments or involve the access of dolomitising fluids, i.e. where access is good then dolomitisation of even the usually resistant fragments will occur.

A simple division of the crinoidal fragments occurring in the limestones can be made: those with, and those without syntaxial rims (pl. 7). The latter are mainly a feature of the micritic limestones as most crinoidal fragments in sparry limestones develop good syntaxial rims (Section 3.2.7). The presence or absence of

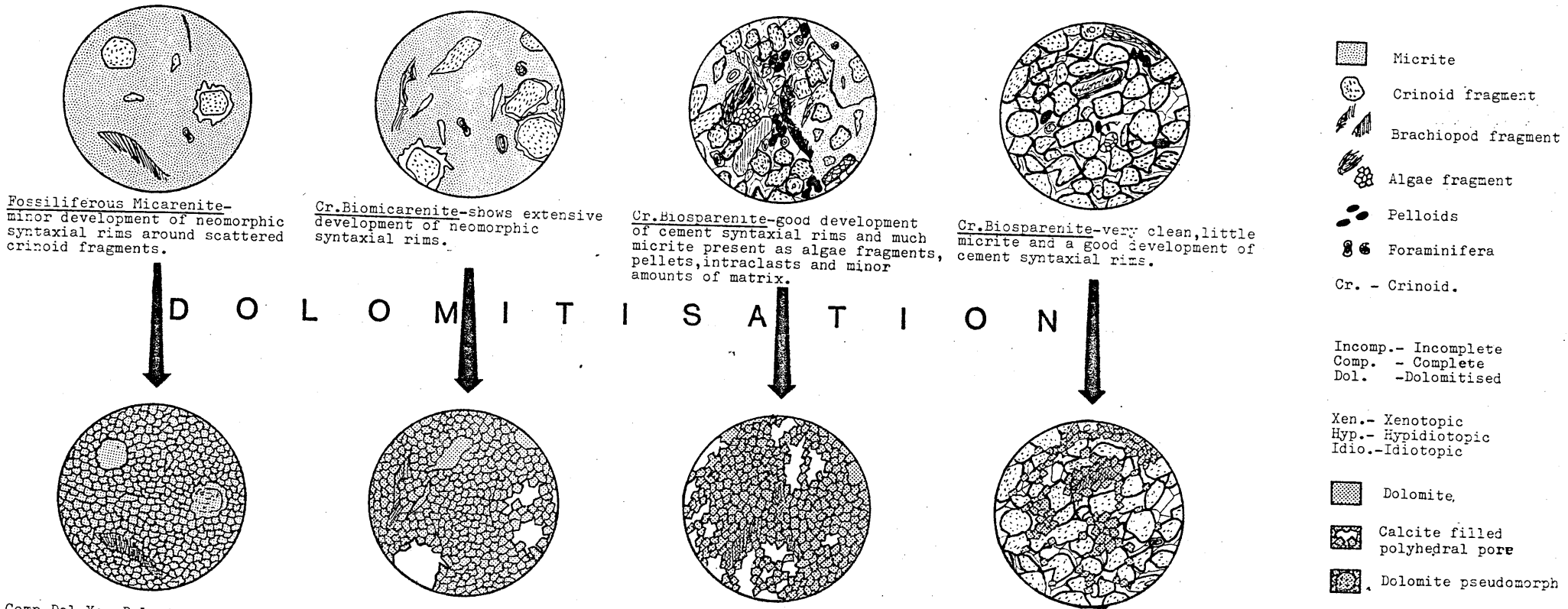


Figure 6 Idealised diagram of the dolomitisation of the various

the syntaxial rims may control whether crinoidal fragments become dolomitised. The existence of syntaxial rims may inhibit dolomitisation, because larger euhedral crystals tend to be less chemically reactive. However, many dolomite pseudomorphs after crinoidal fragments show examples of syntaxial rims. These are indicated by the included nature of the inner crinoidal fragment (Section 3.2.7). Thus the presence of a syntaxial rim would seem to have little effect upon crinoidal susceptibility to dolomitisation. The partially dolomitised crinoidal limestones, however, show undolomitised crinoidal fragments, which are protected by syntaxial rims (Section 4.4.1(4)), formed during cementation by cavity-fill cement. A difference exists between these cement rims and the rims found in the more micritic limestones. The syntaxial rims of the micritic limestones are formed usually by neomorphic aggradation (Section 3.2.7), forming less perfect, more irregular, sporadic rims (pl. 7). A replacement development of a finely-crystalline matrix may lead to an imperfect crystalline rim due to inclusions and imperfect crystallisation. This feature combined with its sporadic and irregular nature may account for the neomorphic rim being more frequently dolomitised. The presence of mouldic vugs and polyhedral pores, however, suggest that some crinoidal fragments did remain resistant within these micritic limestones. This may reflect the occurrence of localised cement syntaxial rims or a better and more perfect development of a neomorphic rim.

The access of dolomitising fluids is also a very important factor when considering the completeness of dolomitisation. As shown by the xenotopic dolostones, where access is good, then even the more resistant material such as crinoids becomes dolomitised, although, considering the above discussion, the xenotopic dolostones may represent former biomicarenites showing no development of neomorphic rims around the crinoids in the limestone samples. It seems likely that the presence of incompletely dolomitised crinoidal fragments is a consequence of both variations in the resistance of certain fragments and the access of dolomitising fluids.

Other types of spar occur within the limestones, such as brachiopod fragments, microsparite and cavity-fill cement, which, if developed sufficiently, may inhibit dolomitisation. The partially dolomitised limestones (Section 4.4.1(4)) show that although brachiopod fragments are resistant to dolomitisation in the early stages of diagenesis these become dolomitised and pseudomorphed as the process proceeds. In the limestones of this study, microsparite formed during neomorphic aggradation (Section 3.2.4) has not developed sufficiently to form resistant areas of sparite, yet, if developed to any great extent, may resist dolomitisation and give rise to polyhedral pores. The sparry cavity-fill cements present a variety of crystal sizes. At their periphery, due to the smaller crystal size, resistance to dolomitisation may be negligible.

However, towards the centre much larger crystals develop and these may resist dolomitisation and form significant amounts of polyhedral pores. The resistance of sparry cement to dolomitisation was noted by Goldberg (1967) in the Hamakhtesh Hagatan dolostones, Israel, but this only appears to be resistant if it consists of non-ferroan calcite. Geochemical microprobe analysis has shown the cavity-fill cements of this study to consist of non-ferroan, low-magnesium calcite and thus they stay resistant to dolomitisation. Sabins, (1962), Neal, (1969) and Al-Hashimi,(1971) have shown that the greater susceptibility of many cavity-fill cements to dolomitisation is due to the presence of Fe^{2+}.

Consequently the porosity of these xenotopic-hypidiotopic dolostones (prior to pore-filling cement) was due not to a molecule for molecule replacement, but to the failure of the dolomitising fluids to totally dolomitise large sparry calcite. This may be a consequence of fluid access and the physical nature of the sparry calcite. The resistant sparry calcite consisted mainly of crinoidal material, probably with well-developed cement or neomorphic syntaxial rims, although well-developed microsparite and cavity-fill cement may have been important. The resistance of these areas has led to the development of mouldic pores and irregular polyhedral pores within an interlocking mosaic of xenotopic dolomite, probably representing a former micritic matrix.

In the limestones the occurrence of abundant crinoidal material is very variable, even within individual beds, and thus upon dolomitisation may lead to local areas having different porosities, and thus weather slightly differently. This may account, in part, for the typical nodular weathering (pl. 14a) and rib-like features (pl. 14b) mentioned in Section 4.1. The variation in these crinoidal-rich limestones may be sufficient to give both crinoidal biomicarenites and sparenites. The biomicarenites would be more easily dolomitised than the more resistant sparenites, due to the presence of cavity-fill cement and cement syntaxial rims. This variability of limestone types in individual beds may explain the pendant-like features and discontinuity of the limestone sandwich seen at the Manystones and High Peak Quarries.

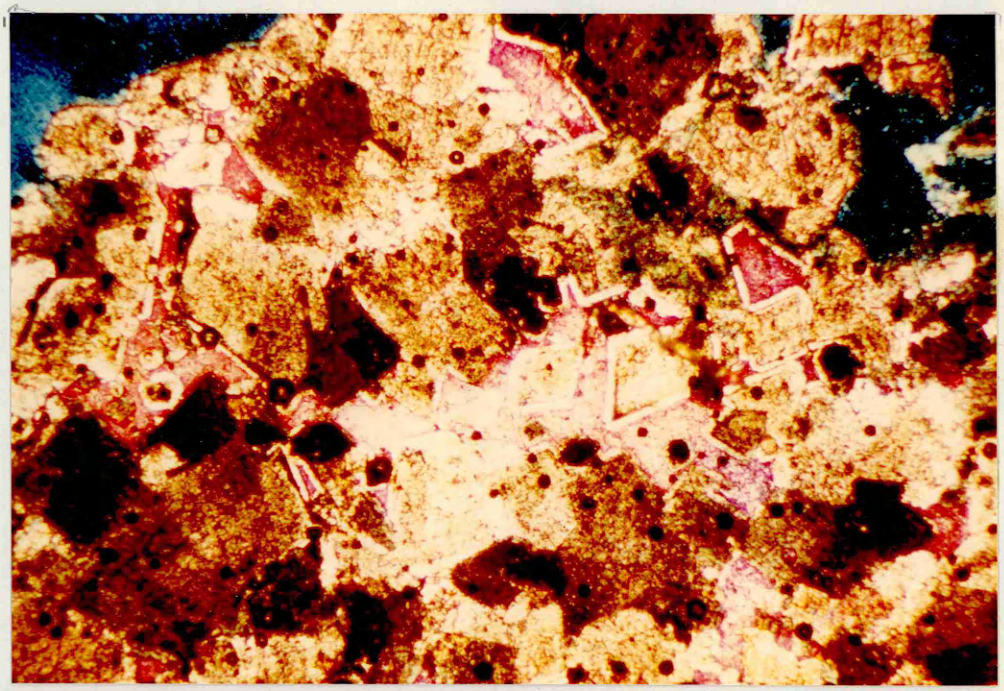
(3) Idiotopic Dolostones

Idiotopic dolostones grade imperceptibly into the incompletely dolomitised xenotopic-hypidiotopic dolostones, probably representing dolomitised crinoidal biosparenites (fig. 6). An increase in the sparry material, such as crinoidal material, in the former limestone, allows more isolated growth of dolomite which will develop more euhedral dolomite crystals (pl. 19a) with abundant porosity. This is quite a marked contrast to the xenotopic and hypidiotopic dolomite of the previous two sections. Weaver (1975) has suggested that the growth of anhedral dolomite may be due to the presence of sulphur. The micrite

material is commonly associated with pyrite and thus may explain the anhedral nature of replacive dolomite. In comparison the sparenites are relatively free of pyrite and thus euhedral dolomite could develop.

The completeness of the dolomitisation does vary quite widely, giving quite a range of primary porosities (Section 5.2). A large, coarse, crinoidal limestone may lead to quite isolated dolomite nuclei and develop a very porous, open, idiotopic dolostone. A decrease in the size of crinoidal fragments will increase the number of dolomite nuclei, allowing quite a tight idiotopic dolomite to develop. Also often included within the fabrics of these former sparenites are areas of finely-crystalline carbonates. Thus the idiotopic dolostones are in fact a mixture of dolostone types, probably including both xenotopic and hypidiotopic textures.

The dominant crystal size of this type of dolostone is between 250 and 300 μ (pl. 19a) as the isolated nature of the nuclei allows the development of quite coarse euhedral dolomite. A less common example of idiotopic dolostones are the finely-crystalline types, which tend to mimic former textures, but are still believed to have a late diagenetic origin. A possible explanation is that they represent the arrest of dolomitisation before an interlocking xenotopic matrix could develop.



a

b

Plate 19 Colour photomicrographs of the dolostone types (a) Idiotopic dolostone with a good development of calcite filled pores and zoning and (b) dolomitic limestone showing scattered dolomite rhombs in a calcitic matrix(pink). x80

(4) Dolomitic Limestone

The dolomitic limestones, having less than 50% dolomite present, are found within and around the dolostone outcrop and can be petrographically divided into two distinct types. Firstly, the dolomitic limestones found at the periphery of the dolostone outcrop, which have scattered dolomite euhedra yet retain much of the limestone's original fabric. Many samples show evidence of unreplaced micrite and in rare cases a "dolomitisation front" (Section 4.4.1(5)). These dolomitic limestones are not a consequence of incomplete dolomitisation due to the resistance of sparry material, but are due to the loss of dolomitising fluids in the latter stages of dolomitisation (pl. 19b).

The second type of dolomitic limestone is a natural progression from the incompletely dolomitised idiotopic dolostone. Crinoidal biosparenites showing good development of cement syntaxial rims have low permeabilities (fig. 6) and thus only scattered dolomite euhedra will develop (pl. 19b).

(5) Mode of Dolomitisation

The dolomitisation process can be identified on three different levels i.e. within the dolostone formation as a whole, within individual beds, and at greater detail within individual crystals.

The access of dolomitising fluids to the dolostone formation appears to have been via jointing, bedding, stylolites, solution channels and fractures. Jointing has been shown to be particularly important in the Wirksworth dolostones (Section 4.3), and gives rise to the very undulatory nature of the dolostone base. Its importance in controlling dolomitisation was also noted by Al-Hashimi (1971) in Northumberland and Freeman (1972) in the Iberian Range, Spain.

From studying the dolomitic limestones around the periphery of the dolostone outcrop, the manner in which dolomitisation occurs can be seen. The front of dolomitisation is seen to be very sharp. Behind the front, dolomitisation is complete, whilst beyond the front (at most a few millimetres) only selective dolomitisation occurs. A slightly higher permeability may develop as dolomitisation proceeds, thus providing access for further dolomitising fluids to the front. It must be remembered that the completeness of dolomitisation will depend greatly on the access of fluids and the fabric of the limestone (Section 4.4.1.). A similar abrupt dolomitisation front has also been noted by Parsons (1922), Nelson (1966), Beales (1953) and Margaritz (1975).

In greater detail, on a crystal basis the dolomitisation appears to occur over a very narrow zone of dissolution-precipitation. Evidence of this is given by the retention of insoluble material which, for example,

outlines the former crinoidal ossicles in the dolomite pseudomorphs. The retention of these structures tends to suggest that dissolution-precipitation occurs over a very narrow zone, thus retaining inclusions in a similar position to that in the original limestones. The lack of any visible textures in the hypidiotopic and xenotopic dolostones, indicating any former textures, suggests that much of the replaced material must have been micritic.

4.4.2. Fossils in the Dolostones

It will be appreciated from the previous sections that the preservation of fossil fragments will depend greatly on the crystal size of the dolostone developed. Certainly the very finely-microcrystalline dolomite is able to replace calcite in the smallest fossils, including foraminifera, ostracods, brachiopod fragments and other small shell fragments, whilst still retaining morphology. However, the great majority of the dolostones are much coarser and thus much of the finer fossil-shell morphology is lost as the dolomite crystals exceed microcrystalline sizes. In hand specimens the fossil fragments are discernible due to the inclusion-free nature, thus appearing slightly paler.

The majority of the fossils in the Wirksworth dolostones are crinoids and brachiopods, although less common rugose and tabulate corals are present. The

finer details of their structure is commonly lost, unless replaced by a slightly finer dolostone which may retain some ornamentation. Usually it is only the coarser features of the organisms that remain, eg. septal plates of corals or brachiopod spines.

Crinoidal fragments, mainly ossicles, constitute the majority of fossil fragments present, particularly in the Hoptonwood Group. It has been noted by many writers (Friedman and Sanders 1967, Murray and Lucia 1967 and Beales 1953) that crinoidal fragments remain undolomitised and upon leaching form good mouldic porosity. In this study, and also noted by Murray (1960) and Lucia (1961), the majority of crinoidal fragments become pseudomorphed by large euhedral dolomite crystals. The central canal is represented by euhedral dolomite similar in size to the matrix of the dolostone, indicating the replacement of a similar lime mud deposited within the canal upon deposition of the ossicle. Dolomite euhedra are also found poikilotopically enclosed within the large pseudomorphs (pl. 18b). During the initial stages of dolomitisation, fluids entered the crinoid fragments along weaknesses, allowing the growth of euhedra within the crinoid fragment, which itself later became altered to dolomite (Lucia, 1961). The euhedra may have nucleated upon the many clays associated with the crinoid structure or upon microdolomitic inclusions formed during the stabilisation from high to low-magnesium calcite (Lohmann and Meyers, 1977).

In the stratigraphically equivalent limestones diagenesis has developed syntaxial rims (cement and neomorphic) around many crinoidal fragments (Section 3.2.7.). These have been argued to affect the crinoids' susceptibility to dolomitisation (Section 4.4.1(2)). The cement and well-developed neomorphic rims remain resistant whilst the poorly developed rims allow dolomitisation to occur. Thus pseudomorphed crinoidal fragments often show syntaxial rims, which have also been noted elsewhere by Murray (1960), Murray and Lucia (1967) and Armstrong (1970). These are identified due to the included nature of the inner fragment. The former stereom structure of the crinoidal fragment becomes occluded upon deposition by carbonate and clay material. This is retained even after dolomitisation and thus distinguishes it from the cleaner syntaxial rim. The retention of this insoluble material in a similar position to that prior to dolomitisation, gives some idea of the process of dolomitisation. Dissolution of calcite and precipitation of dolomite must occur over a very narrow zone, not allowing the clays to escape and thus retaining them in a similar position to the original crinoid. A similar process was proposed by Bathurst (1971) to account for the preservation of detail in recrystallised shells (pl. 6).

4.4.3. Zoning of Dolomite

In many dolostone examples in the Wirksworth area a vague zoning exists because the cloudy centre of the crystal is surrounded by clear crystalline dolomite. A possible explanation is that replacement of micrite and sparite may give cloudy and clearer dolomite respectively; however, no pattern (eg. allochems) to these cloudy areas can be seen. It appears that the slightly less included dolomite is formed as the crystal grows. This may be produced when the dolomitising brines allow a more perfect dolomitisation, which may be more effective in removing insolubles. Evamy (1967) further suggested that some of the inclusions within the dolomite are remnant calcite if so these should decrease as dolomitisation progressed. Another factor that may cause this much cloudier centre, which will be discussed in greater detail later, is centrifugal dolomitisation. This may be associated with calcitic inclusions in the core of the dolomite and release ferric compounds, giving a much cloudier appearance. The presence of these inclusions cannot be shown using Alizarin Red-S stain, however, microprobe analysis does indicate a slightly more calcitic core (Table VI).

The most evident zoning is that occurring around polyhedral pores (pl. 19a). It is not extensively developed, as individual samples show zoned and unzoned euhedra. The zoning usually consists of a shell of dolomite 10-20μ thick, easily identified because of its

clear nature. Microprobe analysis has shown the peripheral zoning to have a similar chemistry to the dolomite of the core, although the comparison is based on only four elements (Table VI).

Many ideas have been suggested for the origin of such zoned dolomite euhedra. Murray (1960) suggested that during the latter stages of dolomitisation a local source of carbonate ions may be required to supply the dolomitising front. Dissolution will occur around euhedra to form a moat of available carbonate ions, and so any further development of the euhedra will grow into the void and produce a clear dolomite. This does not explain the presence of unzoned euhedra, unless we assume these were isolated from later dolomitisation (Wolfe, 1970 and Al-Hashimi, 1971). A similar idea is that dissolution of the remnant calcite occurred in the latter stages of dolomitisation, producing a void into which a cleaner dolomite could grow.

Folk and Siedlecka (1974) suggest that the zoning found in the Precambrian dolostones of Bear Island, Spitsbergen, is due to a change in salinity of the dolomitising fluid. They conjecture that the dilution of the dolomitising fluid promotes the crystallisation of a well-ordered "limpid" dolomite. The origin of the dolomitising brines in the study area is not known, but this model certainly could account for the nature of the zoning.

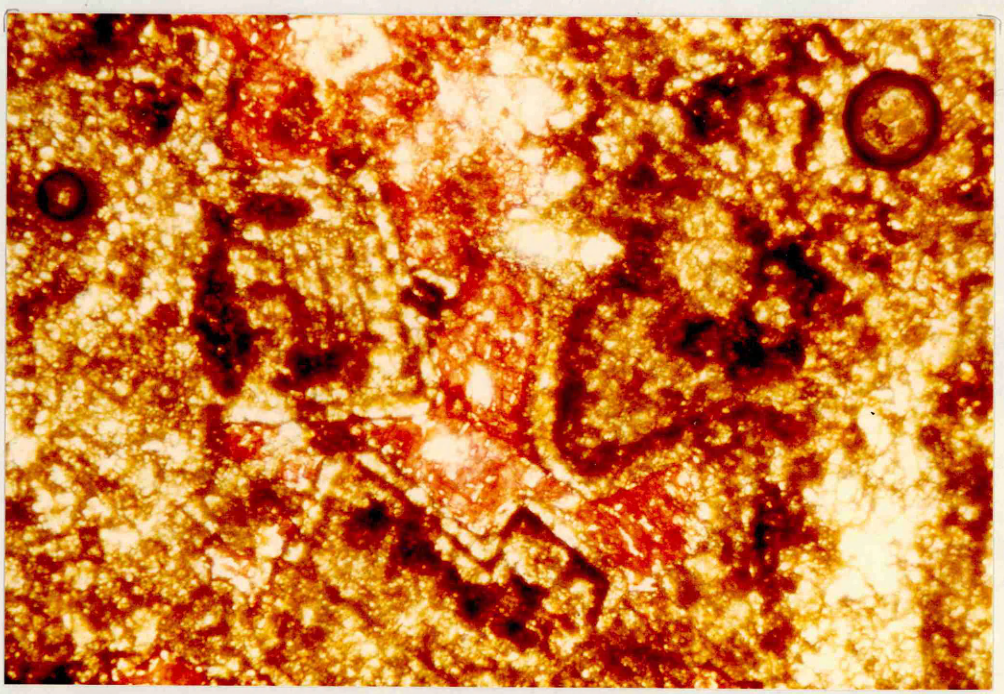
Many of the quite large vugs filled with calcite from the mineralisation are surrounded by dolomite euhedra. This suggests that dolomitisation occurred after mineralisation, whereas elsewhere in the area it is clearly secondary. Within the Magnesium Limestone of Northern England, mineralisation has caused a very localised remobilisation of dolomite around similar vugs(Harwood pers. comm. 1980). A similar process would explain the dolomite euhedra surrounding the mineralised vugs of the Wirksworth area. Thus, there is a possibility that the dolostones were flushed by magnesium-rich fluid, produced by the mineralisation in late Triassic times. The polyhedral pores, which were devoid of calcite , due to leaching during sub-aerial exposure, allowed the deposition of a clean dolomite.

In each of these hypotheses, it is assumed that the unzoned polyhedral pores were isolated during later dolomitisation. Neither the detailed petrography nor geochemistry of the zoning gives any indication of its origin.

4.4.4. Pore-filling Calcite

The dolostones, with the exception of the completely dolomitised xenotopic dolostone, all contain free calcite. This occurs predominantly as a cavity-fill cement, showing a typical cavity-fill texture (pl. 20a) or a single large anhedral calcite crystal (pl. 20b).

a



b

Plate 20 Dolostone cements (a) typical cavity-fill cement in mouldic pore. Harborough Rocks. and (b) single large anhedral calcite crystal filling the ploy hedral pore. Griffe Grange Qu. H. "Group" x80

Prior to present-day leaching, all the mouldic vugs and polyhedral pores were filled with calcite. The calcite has been shown by microprobe analysis to be a non-ferroan, low-magnesium calcite (Table VI) very similar to that found in the limestones, although this does not prove that they have the same source. Many of the mouldic pores have a typical cavity-fill cement (pl. 20a) while the majority of the polyhedral pores show large anhedral crystals. Pray (1969) has noted the reluctance which dolostones have to cementation by groundwater, and so where good clear dolomite occurs, nucleation is poor and large crystals may develop, often completely filling the pore, as seen in the polyhedral pores of this study. Also, slow crystallisation from dilute meteoric water may account for the large crystals but does require the low nucleation noted by Pray. The typical cavity-fill cement of the mouldic pores probably represented greater nucleation due to the less perfect nature of the dolomite surrounding the mouldic pores.

As described earlier, many polyhedral and mouldic pores are believed to represent incomplete dolomitisation of crinoidal fragments. Thus immediately after dolomitisation the pores are filled by remnant limestone. This is believed to have been removed by leaching, as no remnant textures can be seen in any of the many thousands of pores that have been studied.

4.4.5. Dedolomitisation

A distinct and very important feature of these dolostones is the considerable amount of corrosion of the dolomite around calcite-filled pores. This is caused by dedolomitisation and is identified by the use of the organic stain Alizarin Red-S.

The dolomite is seemingly replaced by calcite with the former shape of the dolomite rhombs being outlined by inclusions in the calcite or by small remnants of dolomite. The process was first discussed by Von Morlot (1847) with the exception of Cayeaux (1935), the process has received little attention, up until the last three decades.

The last thirty years have produced a relative wealth of literature dealing with every aspect of the process and include papers by Faust (1949), Tatarskii (1949), Khvorova (1958), Lucia (1961), Shearman et al. (1961), Braddock and Bowles (1963), Evamy (1963), Schmidt (1965), Evamy (1967), Friedman and Sanders (1967, Goldberg (1967), Shearman and Shirmohammadi (1969), Braun and Friedman (1969), Folkman (1969), Wolfe (1970), Al-Hashimi and Hemmingway (1973), Katz (1971), Zenger (1973) and Longman and Mench (1978). The finest documented examples of dedolomitisation have been given by Shearman et al. (1961) and Evamy (1967) in the dolomites of the Jura. These show almost total dedolomitisation and additional occurrences have been described by Khvorova (1958), Folkman (1969) and

Al-Hashimi and Hemmingway (1973). The evidence in the published accounts that the parent rocks were dolostones includes (i) the presence of remnant dolomite, usually within large anhedral calcite crystals, (ii) rhombic calcite (although challenged by Perkins (1969) due to the description of primary rhombic calcite) (iii) ghosts of rhombs due to inclusions (iv) aggregates of small calcite crystals having a rhombic outline (v) rhombohedral pores and (vi) greumeleuse or clotted texture.

The dolostones of this study show partial dedolomitisation rather than total dedolomitisation as described above. Around the calcite-filled polyhedral pores some corrosion of dolomite occurs and tends to be restricted to these areas. This type of dedolomitisation has received less attention in the literature, but has been found to play a significant role in the development of porosity in the dolostones of this study.

The dedolomitisation is primarily associated with calcite-filled polyhedral pores and, depending upon the presence or absence of zoning, can develop two different types of texture. Examples in every stage of alteration can be found, varying from slightly altered to totally replaced crystals, depending upon localised conditions. Dedolomitisation is believed to be a continuous process, but for descriptive purposes, it has been divided into

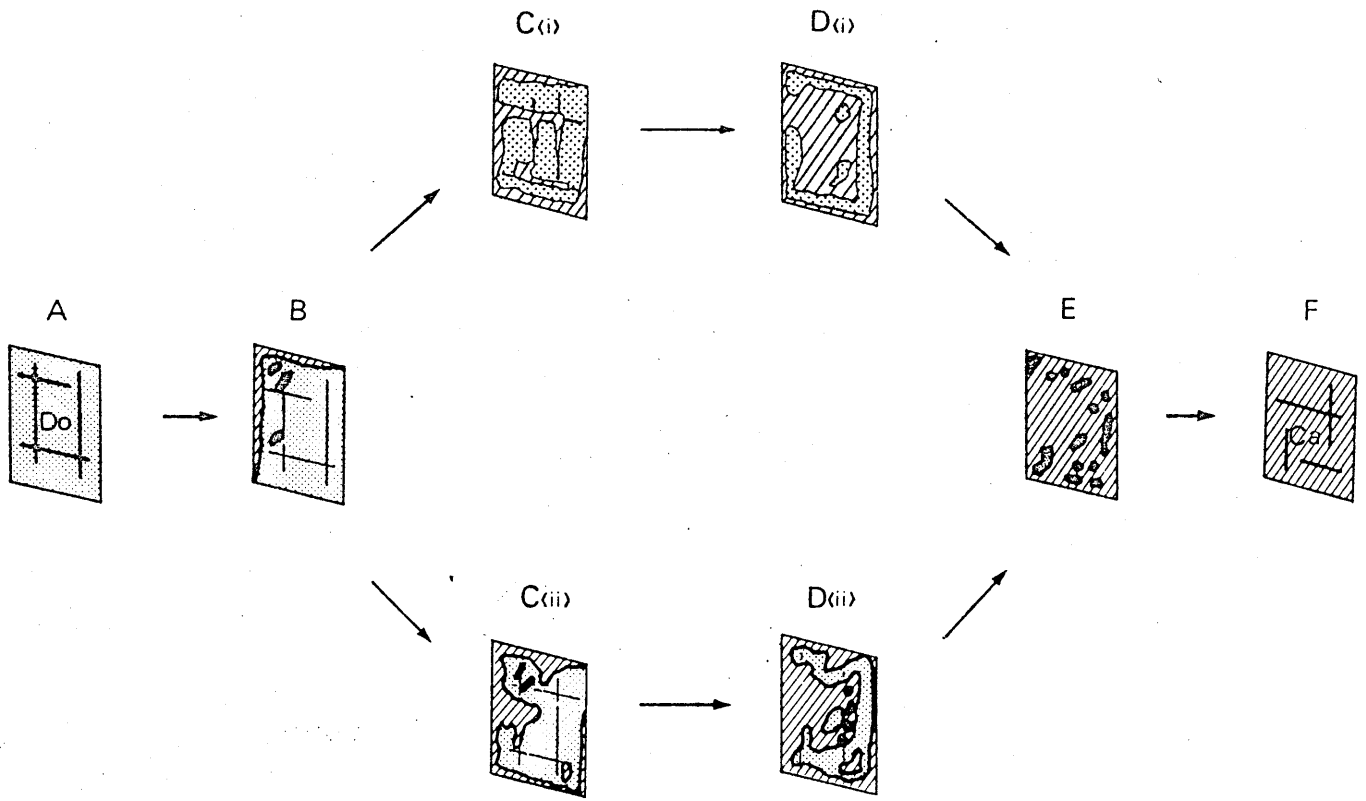
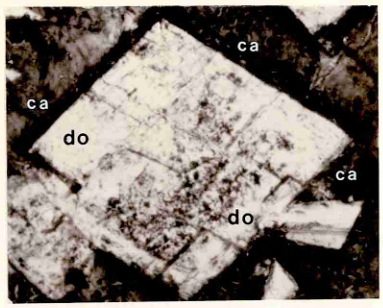


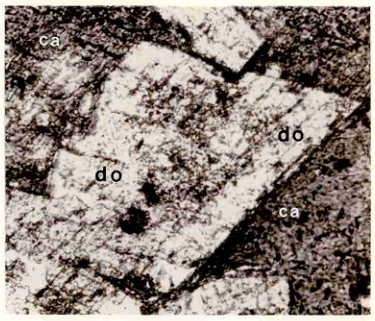
Figure 7 A diagrammatic sequence of the dedolomitisation : A,unaltered outline; B,centripetal corrosion of dolomite; C(i),growth of the calcite along weaknesses such as cleavage, C(ii), small embayments of calcite into the dolomite; D(i),relic rim dolomite, D(ii), larger areas of calcite protruding into the dolomite; E,remnants of dolomite surrounded by calcite; F,dedolomite calcite.

Plate 21 A series of photographs illustrating the dedolomitisation process. A,An euhedral dolomite crystal surrounded by calcite but showing no significant alteration; B,slight corrosion of the e euhedra along cleavages; C(i), dolomite euhedra(at extinction) surrounded by calcite and showing a small embayment of calcite into the dolomite; C(ii), growth of calcite into the dolomite along cleavage planes; D(i) further dedolomitisation to give irregular area of dolomite; D(ii) skeletal dolomite,the outer rim remaining; E, remnants of dolomite(anhedra) surrounded by calcite; F, consists entirely of calcite but showing ghosts of rhombs,due to inclusions. x80



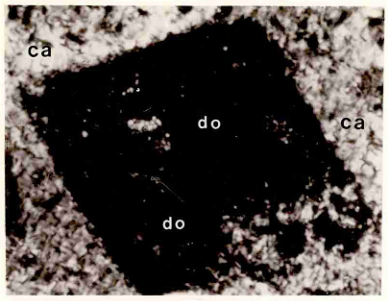
A

100μ



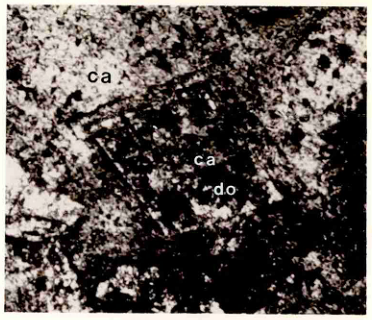
B

100μ



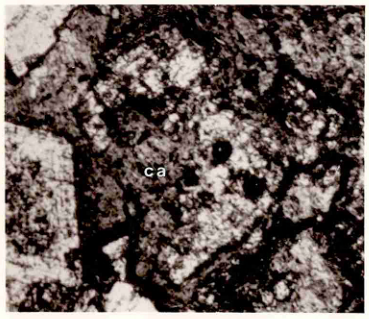
C(i)

100μ



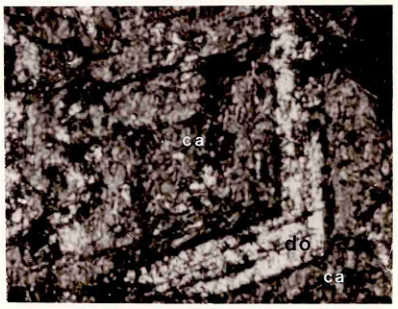
C(ii)

100μ



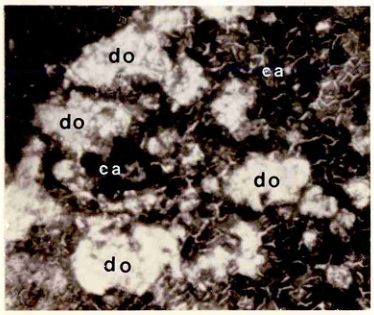
D(i)

100μ



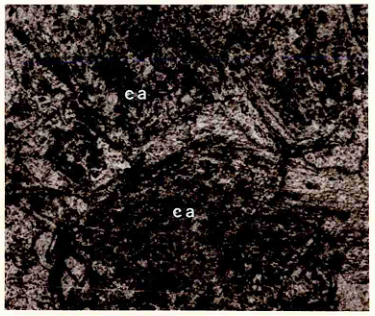
D(ii)

100μ



E

100μ



F

100μ

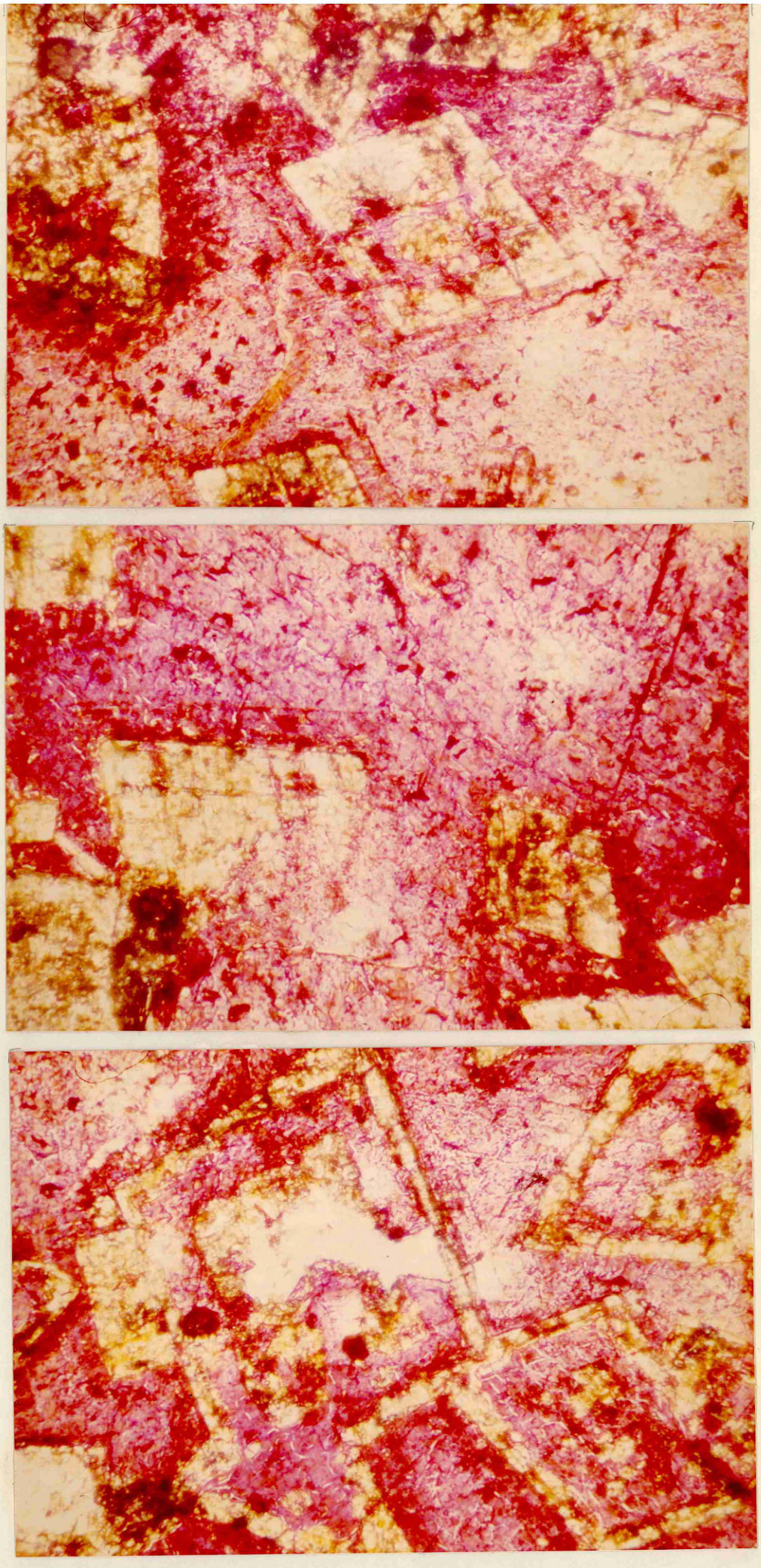
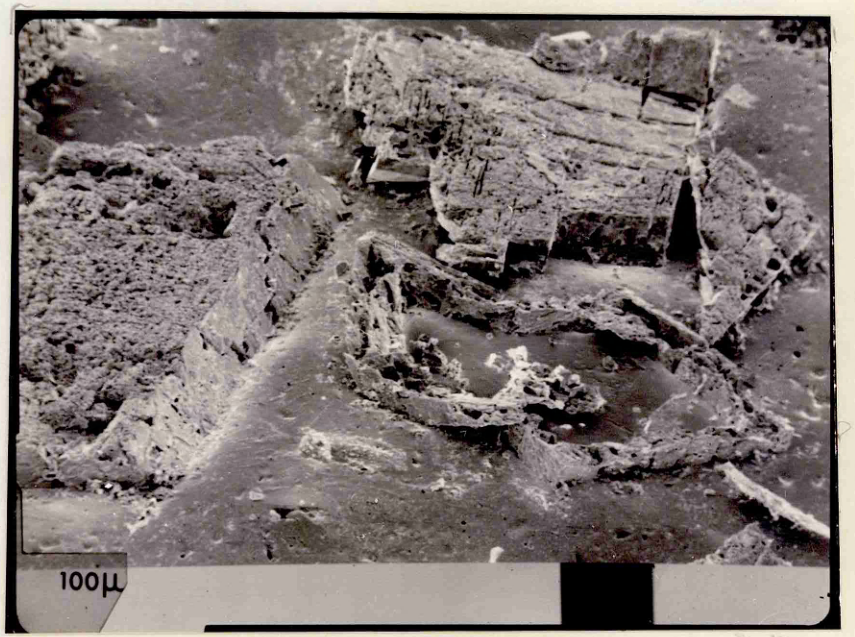


Plate 22 Colour photomicrographs of dedolomitisation(a) calcite(pink) intruding along cleavages or(b) as embayments into the centre of the crystal and (c) further dedolomitisation to give skeletal dolomite. x200

a



b

Plate 23 Photographs of polished S.E.M. samples which have been etched with dilute acid to partially remove the calcite and reveal the remnant textures. (a)corroded dolomite euhedra and (b) skeletal dolomite,both textures being due to dedolomitisation.

six stages (A-F). These stages, illustrated in Plate 21, fig. 7, comprise the following:

(A) unaltered euhedral dolomite crystals occurring either at the edges of polyhedral pores within a xenotopic matrix, or more isolated euhedra of an idiotopic dolostone (fig. 7a, pls. 21a, 22).

(B) during the initial stages of alteration the dolomite may be attacked at its edges, producing centripetal corrosion (fig. 7b, pls. 21a, 22a, 23a). This will tend to be more evident in the unzoned dolomite, due to the more resistant nature of the zoning. At this early stage, but more evident later, the dolomite is in optical continuity with the pore-filling calcite, thus dedolomitisation continues by a syntaxial growth of the calcite crystals. A similar process was described by Khvorova (1958) and Shearman et al. (1961) eventually giving a dedolomite of coarsely-crystalline calcite.

(C) the corrosion continues towards the centre of the crystal via weaknesses such as cleavage (fig. 7c(i), pls. 21c(i), 22b), or as embayments (fig. 7c(ii), pl. 21c(ii)). The zoning remains fairly resistant and if access is gained to the central area of the crystal then centrifugal dedolomitisation occurs, due to the less resistant nature of core (possibly from the presence of remnant calcite inclusions). The replacive calcite crystals at this stage have a

number of orientations due to replacement of various calcite crystals, forming from adjacent crystals in the pore-filling cement or inclusions within the core.

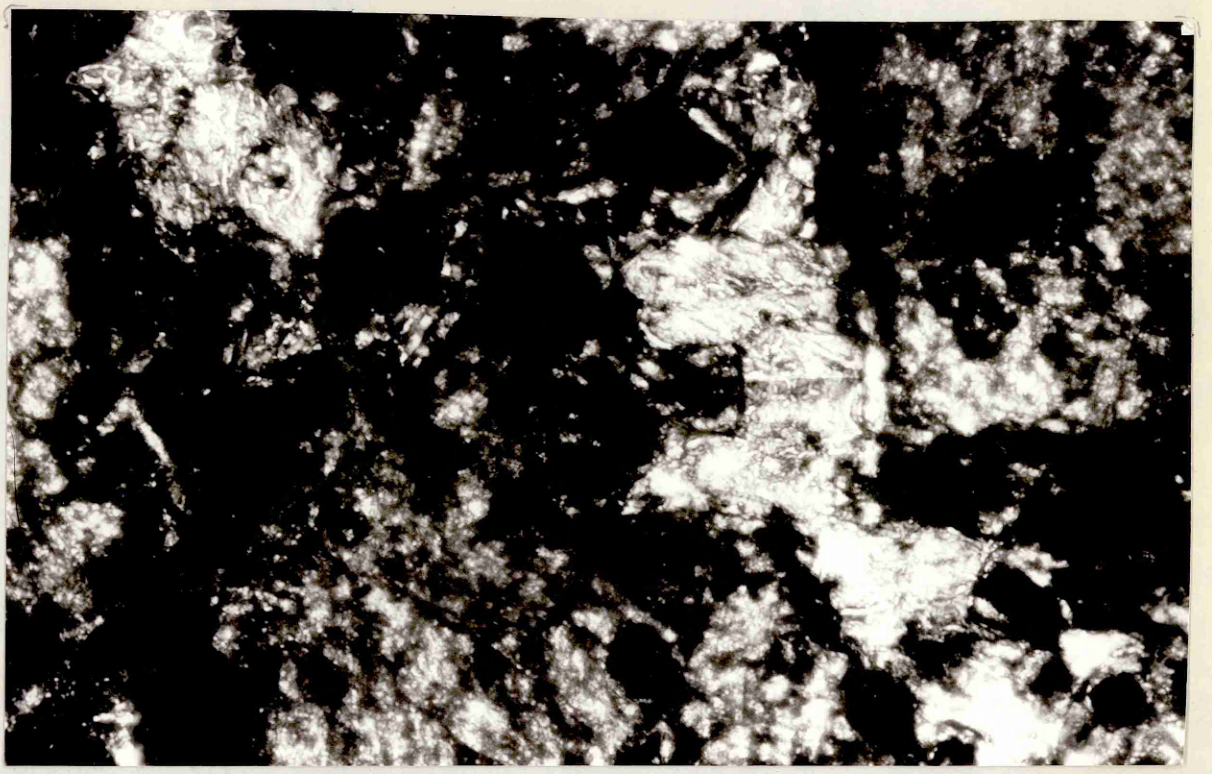
(D) further attack leads to the development of skeletal dolomite, which is seen particularly well where the cores of zoned dolomite have become totally dedolomitised (fig. 7d, pl. 21d, 22c, 23b) Even at this stage the outer zone has retained much of its original shape.

(E) additional alteration leads to the development of a fairly coarse sparry limestone with many small dolomite remnants (fig. 7e, pl. 21e), similar to those described by Shearman et al. (1961).

(F) total alteration wiil lead to a dedolomitic limestone, consisting of coarsely-crystalline calcite, possibly showing some evidence of the former dolostone. In this study dedolomitic limestones are not found with the features described above. The dedolomitic limestones of this study are found adjacent to mineral veins and in partially dolomitised limestones, where scattered rhombs have become totally dedolomitised in many cases marked by rhombic moulds. The former dolostone texture is indicated by ghosts of insoluble material, outlining the former textures (fig. 7f, pl. 21f). Many examples of the replacive dedolomitisation around polyhedral pores show no

ghost textures, but do commonly have dolomite remnants that can indicate the former extent of the rhomb. These differences in preservation probably reflect the contrasting modes of dedolomitisation (Section 4.4.5(i)).

The syntaxial development of the pore-filling calcite during dedolomitisation makes it difficult to decide whether dedolomitisation occurred during recent weathering, or prior to precipitation of cavity cement. Thus, could dedolomitisation be a feature of an earlier sub-aerial exposure, the calcite of which has been removed and later infilled by the present cavity-fill cement? Microprobe analysis has indicated that close to the dedolomitisation, calcite may have quite high amounts of magnesium (8.1%), whilst away from the dedolomitisation the cavity-fill cement has much lower values (0.7%) (Table VI). Evamy (1967) and Al-Hashimi and Hemmimgway (1973) have suggested that high-magnesium will remain after dedolomitisation due to the presence of a high magnesium content in the precipitating solution. Low-magnesium calcite, similar to that found as pore-filling calcite cannot form due to the inhibiting effect of the high magnesium content of the fluid (Bischoff 1968) which must be present after dedolomitisation. This causes the deposition of high-magnesium calcite, as shown in this study, or aragonite which was shown by De Groot (1967) to occur in his experiments. Further evidence of this high-



a

b

Plate 24 Ferric material, probably ferric hydroxide, associated with dedolomitisation (a) photomicrograph of dedolomitisation indicated by the opaque ferric material. Griffe Grange Qu. x200 and (b) a rusty crust of dedolomitisation associated with jointing, the dedolomitisation has become leached to form grikes. Acre Limestone, Beadnell, Northumberland.

magnesium calcite is the susceptibility which dedolomite calcite has to solution, indicating the carbonate's higher solubility. This high-magnesium calcite seems to suggest that dedolomitisation is occurring at outcrop today.

The dedolomitisation textures described, above all, show an association with ferric material (pl. 24a), giving the dolostone its yellowish-brown coloration. The iron content of the dolostone (av. 0.47%) has become oxidised during dedolomitisation forming the more insoluble ferric compounds. This association of ferric material with dedolomitisation is beautifully displayed by the dolomitised Acre Limestone at Beadnell, Northumberland (pl. 24b), and is due to the ferroan nature (3.15%) of the former dolostones. The ferric material has been shown by Al-Hashimi and Hemingway (1973) to consist mainly of ferric hydroxide.

A second type of dedolomitisation is evident in these rocks and has recently been described by Munn and Jackson (1980). It is found associated with large anhedral crinoidal dolomite pseudomorphs. Incomplete dolomitisation of crinoidal fragments, and later leaching, will produce mouldic pores. However, many of the pores show a remnant rim of optically continuous dolomite (pls. 25e, 26), particularly good examples are seen at Harborough Rocks. These are not believed to be caused by a peripheral pseudomorphing described by Lucia (1961), but can be

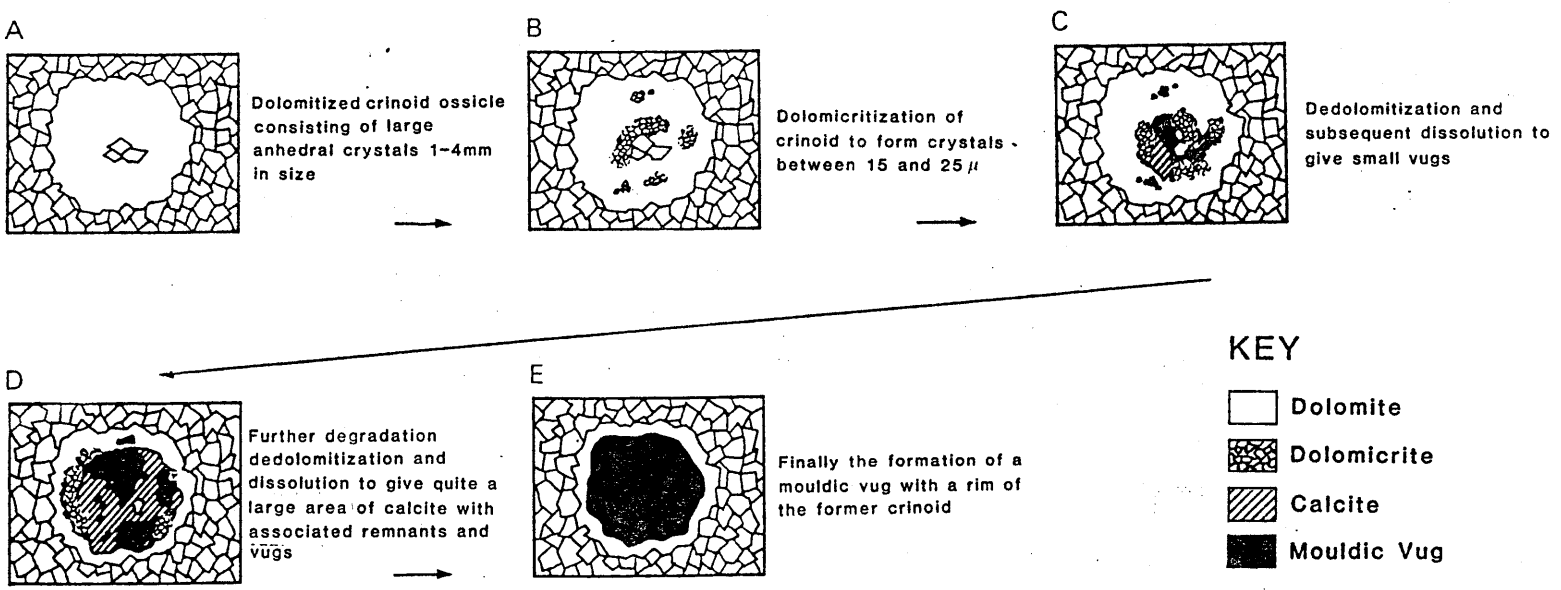
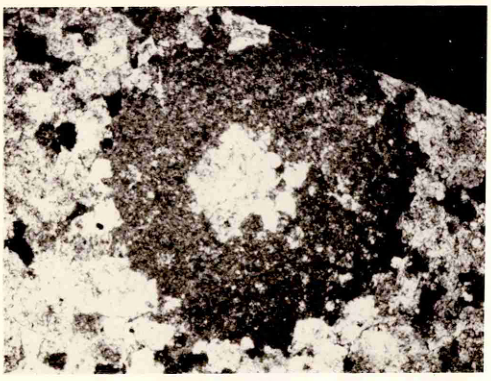


Figure 8 Schematic diagram of the development of mouldic porosity due to the diagenesis of dolomitised crinoid ossicles.

Plate 25 Photographs illustrating the diagenesis of the dolomitised crinoid ossicles to give the characteristic mouldic porosity A, Large anhedral crystal with central dolomite euhedra representing the former central lumen of the ossicle; B, anhedral dolomite with the included dolomicrite; C, porosity developed due to the solution of calcite; D, mouldic vug showing some optically continuous dolomite; E, characteristic mouldic porosity. Photomicropgraphs x20

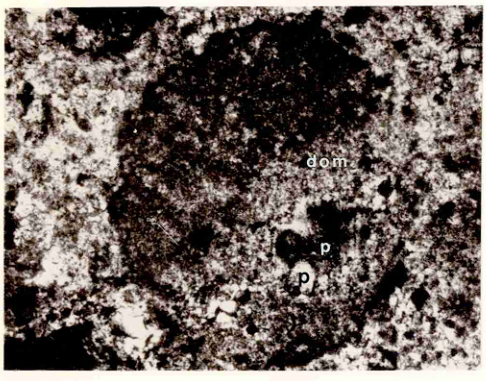


A

1mm

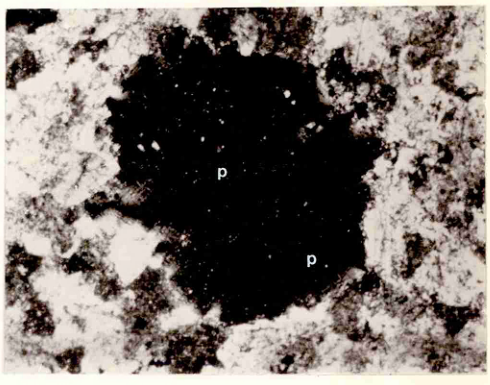
B

1mm



C

1mm



D

1mm

E

2cm

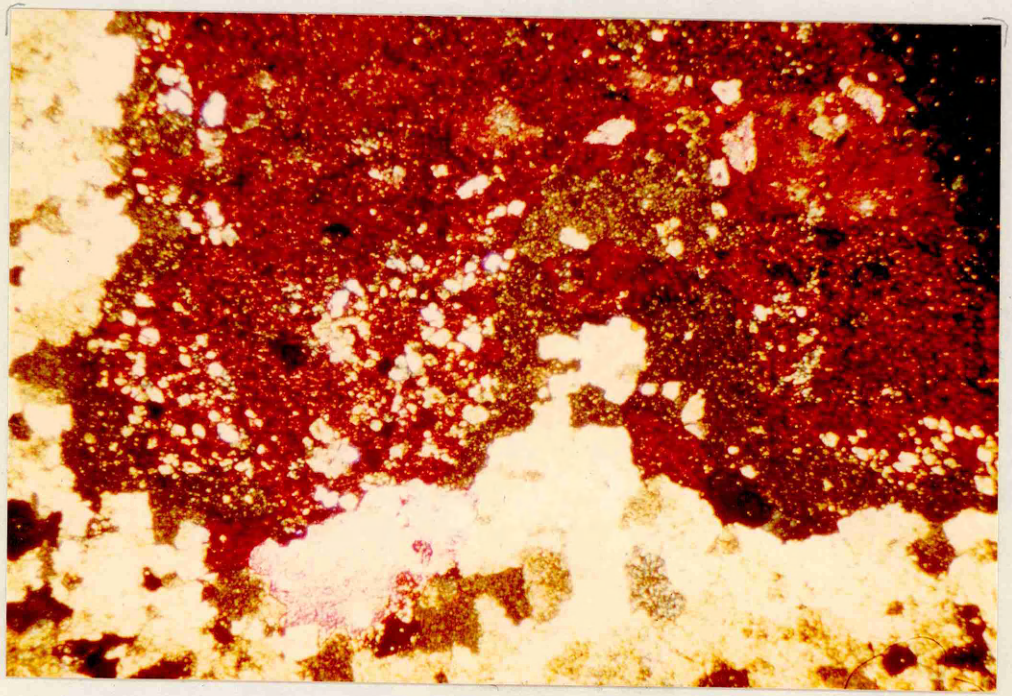


Plate 26 Dedolomitisation of crinoidal pseudomorph - a colour photomicrograph, showing the regeneration of a single large calcite (pink) crystal with dolomite remnats and remnant rim. Harborough Rocks. H."Group" x20

shown to occur by dedolomitisation of a central crinoid pseudomorph, the remnant rim representing the replaced syntaxial rim.

The crinoid dolomite pseudomorphs commonly show a degradation of crystal size towards their centres, giving a dolomicrite (5-15u)(pl.25b). Where dolomitised syntaxial rims are present, these appear quite resistant to dolomicritisation which is found to be a principal reason for their resistance to leaching. The dolomicritisation can be seen to be widely associated with dedolomitisation (fig.8, pls.25,26) which will cause the eventual removal of the pseudomorph, apart from the presence of the more resistant syntaxial rim. Thus, it is the dolomicritisation which controls the stability of these large pseudomorphs.

The dolomicritisation is thought to be caused by stress in accordance with that described by Orme and Brown (1963) but only causes degradation of the central fossil pseudomorph. This suggests that there exists a structural difference between pseudomorphed crinoids and syntaxial rims. The susceptibility of the crinoidal pseudomorph to stress is probably inherited from the former ossicle. Examples of micritised crinoid ossicles (grain diminution, Section 3.2.8) occur in the unaltered limestones, these are far less common than the dolomicritised pseudomorphs and thus would not appear to be caused by mimicing of a former texture.

The original crinoid fragment consisted of a very porous stereom structure (Raup, 1959, who reported a porosity of 60%) prior to its infilling during diagenesis by finely-crystalline carbonate and clays, and gives the characteristic included appearance of these fragments. Some conjecture existed, whether the crinoidal structure represented a single crystal or a polycrystalline aggregate of optically continuous calcite. Towe (1967) clarified the problem when he described such plates as being a mixture of crystal size, essentially a single crystal but consisting of an external polycrystalline aggregate around its growing edge. Other instances of early alteration of crinoids has been described by Neugebauer (1978). Degradation of the large crinoidal calcite crystals may occur during the mineralogical stabilisation of high-magnesium calcite to low-magnesium calcite during diagenesis.

Stress during early compaction may also introduce heterogeneities into the crinoid structure prior to diagenesis. Thus, there are a number of ways to introduce heterogeneity into the crinoid plate and these may account for the degradation of the original limestones by stress (Section 3.2.8.).During dolomitisation many of these flaws may have been preserved, and due to the more brittle nature of dolomite, relative to limestone, even greater degradation will occur once the fragments have become stressed.

Dolomicritisation increases the surface area of the dolomite crystal mosaic, which in turn increases its reactivity, causing a greater susceptibility to dedolomitisation. Many pseudomorphs show degradation but far less are affected by dedolomitisation. Dedolomitised crinoidal pseudomorphs tend to be associated with samples having free calcite (calcite-filled pores). The dedolomitisation of crinoidal pseudomorphs appears to be a result of this local source of Ca^{2+}, but even within these samples, non-dedolomitised pseudomorphs exist. Therefore, there exists a further control, that is, access of fluids to the centres of dedolomitisation. This accounts for the lack of dedolomitisation in the xenotopic dolostones. The dedolomitisation calcite can be shown to regenerate a single calcite crystal (pl. 26b) often enclosing many dolomite remnants, indicating a dedolomitisation origin, rather than incomplete dolomitisation described by Lucia (1961). Microprobe analysis has shown that this dedolomitisation calcite is not composed of high-magnesium calcite, but of low-magnesium calcite with quite a high remnant magnesium content (1.94%). However, closer to the dolomite much higher magnesium values (5.74%) can be found and would appear to suggest that dedolomitisation is occurring in present-day vadose zones, which may account for the very common occurence of mouldic vugs in these dolostones, particularly at Harborough Rock.

The variable magnesium content in the dedolomitisation calcite of the crinoidal pseudomorphs may indicate:

(a) both the high and low-magnesium calcite are products of the presently-forming dedolomitisation. This process allows stabilisation of formerly deposited high-magnesium calcite, contemporaneously with further dedolomitisation. The saturated solutions required to cause dedolomitisation, although saturated with calcite, remain undersaturated with respect to high-magnesium calcite, due to their slightly different solubilities. This would allow the stabilisation of high-magnesium calcite to low-magnesium calcite by dissolution-reprecipitation, yet causing no undersaturation of the solution and thus dedolomitisation could still occur.

(b) the calcite represents two phases of dedolomitisation. The earlier phase has become stabilised to low-magnesium calcite with its high magnesium content, indicating the pre-existence of high-magnesium calcite. Under present-day weathering a second phase of dedolomitisation has begun depositing high-magnesium calcite syntaxially upon the former calcite. Thus it may be considered that some of the dedolomitisation associated with the polyhedral pores may have an earlier origin.

(c) the lower-magnesium calcite may represent a former cavity-fill cement which has promoted dedolomitisation at its peripheries due to present-day weathering. This does not account for the relatively high magnesium

content, which may exceed 8%, as most cavity-fill cements in these dolostones show much lower magnesium calcite.

Due to the lack of information concerning the crystallisation of dedolomite calcite, and no indication of two phases of calcite in thin sections, it was beyond the scope of this study to determine the cause of dedolomitisation in the crinoidal pseudomorphs.

A sequence of dolomicritisation, dedolomitisation and finally leaching (fig 8, pl. 25) leads to the development of mouldic vugs. Any syntaxial rims that are present remain as resistant, optically continuous rims. Pseudomorphs showing no development of a syntaxial rim would lead to the development of a mouldic vug undistinguishable from those formed by incomplete dolomitisation.

(1) Mode of Dedolomitisation

Yanat'eva (1955) and De Groot (1967) have shown that at high pCO_2 (partial pressure of carbon dioxide) congruent dissolution of dolomite occurs (fig. 9a), whereas at lower pCO_2 incongruent dissolution occurs to give calcite and a magnesium-rich fluid (fig. 9a). Yanat'eva studied the influence that calcium sulphate may have upon the reaction. She found that when the pCO_2 was high, calcium sulphate was inert, but it enhances the dolomite's incongruent solubility at low pCO_2 and this

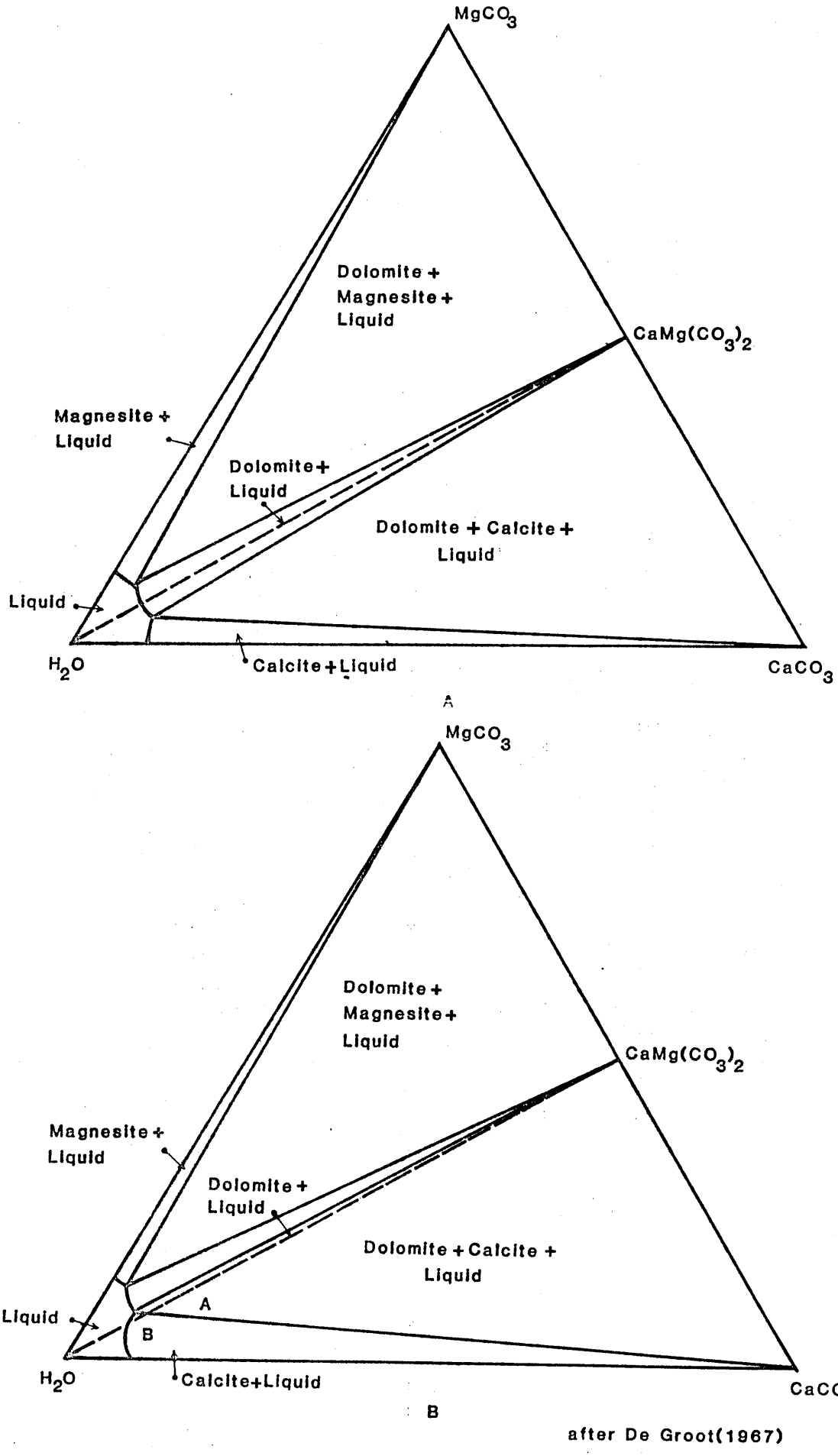


Figure 9 A, High pCO_2; dolomite dissolves congruently. Addition of water to dolomite produces solution in equilibrium with dolomite. B. Low pCO_2 dolomite dissolves incongruently. Addition of water to dolomite produces either, (i) solution in equilibrium with dolomite or calcite, or (ii) in equilibrium with calcite.

was confirmed by De Groot's experiments. The relationship which dedolomitisation has with calcium sulphate was suggested as early as 1848 by Von Morlot and has since become a major factor in explaining the occurrence of dedolomitisation, due to the very common association dolostones have with evaporites.

De Groot's (1967) experiments, although confirming much of Yanat'eva's work, went much further and studied the effect of other variables such as the rate of flow and temperature upon the reaction. He concludes that the conditions for effective dedolomitisation require:

1) a high rate of water flow to remove Mg^{2+} formed, thus keeping the Ca/Mg ratio of the water constantly high. This may explain to a certain degree the low magnesium nature of the dedolomitised crinoidal pseudomorphs.

2) a carbon dioxide partial pressure considerably lower than 0.5 atms..

3) temperatures not higher than $50^{o}C$.

These conditions point to a near-surface origin for dedolomitisation, as noted by many writers, most of whom explain dedolomitisation as occurring under sub-aerial conditions, either in calcium sulphate-rich groundwater (Tatarskii 1949, Khvorova 1958, Shearman et al. 1961,

Braddock and Bowles 1963, Goldberg 1967, Wolfe 1970 and Zenger 1973) or sulphate-rich waters derived from the oxidation of pyrite (Folkman 1969, Zenger 1973 and Jacka 1977). Many occurrences can be related to either present-day weathering surfaces or ancient unconformities (Schmidt 1965, Braun and Friedman 1969 and Wolfe 1970). Geochemically it has been shown that meteoric waters have been involved during dedolomitisation by the study of oxygen and carbon isotopes (Fritz 1967) and strontium depletion (Shearman and Shirmohammadi, 1969). Thus it seems likely that most examples of dedolomitisation can be proven to be a near-surface process. The dedolomitisation of this study is believed to be mainly a modern feature related to the present-day weathering profile, either within the phreatic or vadose zones.

The phreatic zone has been favoured by many writers, as the zone of greatest dedolomitisation. In this environment the dissolution of calcium sulphate may enhance the effectiveness of the process as noted by Yanat'eva and De Groot. The major source of calcium sulphate is gypsum or anhydrite. In the Wirksworth area no evaporites are known in the limestone succession, yet evaporites have been recorded in the Hathern borehole (Llewellyn and Stabbins 1970) to the east of the area in the Widmerpool Gulf. These may provide significant amounts of calcium sulphate to the groundwater, making the phreatic zone an effective zone of dedolomitisation. A more localised source of sulphate may be the oxidation

of pyrite associated with the micritic limestones and clay wayboards. Thus we have an ideal situation for dedolomitisation to occur, having sufficient flow, calcium saturation and calcium sulphate. Under these conditions widespread dedolomitisation would be expected, probably very similar to that found by Shearman et al., (1961) and Evamy (1967). However, the dedolomitisation of this study is much more localised, occurring mainly around calcite-filled polyhedral pores. This suggests that, either access within the phreatic zone is limited and only allows localised dedolomitisation to develop or that a zone of more localised saturation, such as that occurring in the vadose zone, exists.

Langmuir's (1971) study of the groundwaters in a dolostone formation in central Pennsylvania, discovered incongruent dissolution of dolomite giving excess Mg^{2+} to the groundwater. Wigley (1973) has shown that at low temperature ($10^{o}C$), calcium-rich dolomite will dissolve incongruently in the presence of a saturated meteoric solution. However, the behaviour of ideal dolomite is not certain, even though some natural dolomites indicate incongruent dissolution. De Groot (1967) also notes that it is the high Ca/Mg ratio that becomes important and that even sea water with its high Mg^{2+} content may cause dedolomitisation. Al-Hashimi and Hemmingway (1973) suggest that modified seawater may play a significant part in the dedolomitisation of

the dolomitised Acre Limestone of Beadnell, Northumberland.

It is suggested that aggressive meteoric waters (Section 5.3.) present in the vadose and active phreatic zones (fig. 3) may penetrate along the calcite-dolomite junction of the calcite-filled polyhedral pores, and become saturated by the dissolution of the calcite. Under surface conditions this would allow incongruent dissolution of the surrounding dolomite, depositing high or low-magnesium calcite, syntaxially upon the pore-filling calcite. The very restricted nature of the environment would appear not to allow a rapid movement of fluids and thus loss of magnesium. This means that high-magnesium calcite or aragonite (De Groot 1967) would be deposited due to the inhibiting effect of Mg^{2+} (Bischoff 1968). Access within the dolostones may be increased during dedolomitisation due to contemporaneous leaching by the same undersaturated waters that later become saturated and causes dedolomitisation.

The active (aggressive) phreatic zone presents an ideal chemical environment for the development of this dedolomitisation. Here a constant supply of aggressive water can be maintained in direct contrast to the vadose zone. Maximum dedolomitisation would be expected to occur where the supply and flow of water is greatest, that is along channels, jointing, bedding, stylolites and fractures. The dedolomitisation, although at its maximum in these areas, would be controlled largely by

the fabric of the dolostone i.e. dedolomitisation could only be rife in samples having some calcite. For example, the xenotopic dolostones would remain unaltered in the great majority of cases, whilst a more idiotopic dolostone may show extensive dedolomitisation. It is thought that these conditions would cause a more pervasive dedolomitisation due to its saturated nature.

It can be shown geochemically that the surface enhancement of dedolomitisation and the enhanced mouldic porosity of the face of Harborough Rocks (Section 5.3.4.), that dedolomitisation does occur in the vadose zone, where supply of aggressive waters is sufficient along channels etc., and close to the surface due to seepage of carbon dioxide-enriched waters coming from the soil (Section 5.3.5.). These surface examples of dedolomitisation give evidence of dedolomitisation being quite active in the vadose zone at the present-day surface. Periodically rainfall will allow extensive penetrations of the dolostones by aggressive water,to allow dedolomitisation. The localised nature of the dedolomitisation in these dolostones would be more ideally accounted for in the vadose zone.

A characteristic of the vadose zone is the localised and sporadic nature of the saturation. The major controls of groundwater in the vadose zone are the karst channels, joints, e.t.c., and far less saturation will occur in the bulk of

the rock not penetrated by jointing, bedding, etc., thus allowing limited leaching and dedolomitisation, which is a characteristic of the dolostones of the study. Due to the saturated nature of the active phreatic zone more extensive dedolomitisation, within the bulk of the dolostones, would be expected to occur. In both zones the greater leaching and dedolomitisation associated mainly with jointing and bedding would be expected. Thus from the distribution of dedolomitisation it appears that the major development of dedolomitisation has probably occurred in the vadose, although it is possible that some of the dedolomitisation may be related to an earlier diagenesis in the phreatic zone and may be occurring at depth today in the Wirksworth area.

Figure 10 shows an idealised profile through a dolostone formation, indicating a wide variation in its fabric and dedolomitisation. Abundant dedolomitisation may be found at the surface due to aggressive waters emanating from the overlying soil and within the formation adjacent to karst channels such as bedding, jointing and fractures where a good supply of aggressive water is present. The extent of dedolomitisation in these favourable areas depends greatly on the fabric of the dolostone and particularly on the amount of pore-filling calcite present. In this situation an incompletely dolomitised, calcite-rich hypidiotopic or idiotopic dolostone could develop a very extensive dedolomitisation and become almost totally dedolomitised.

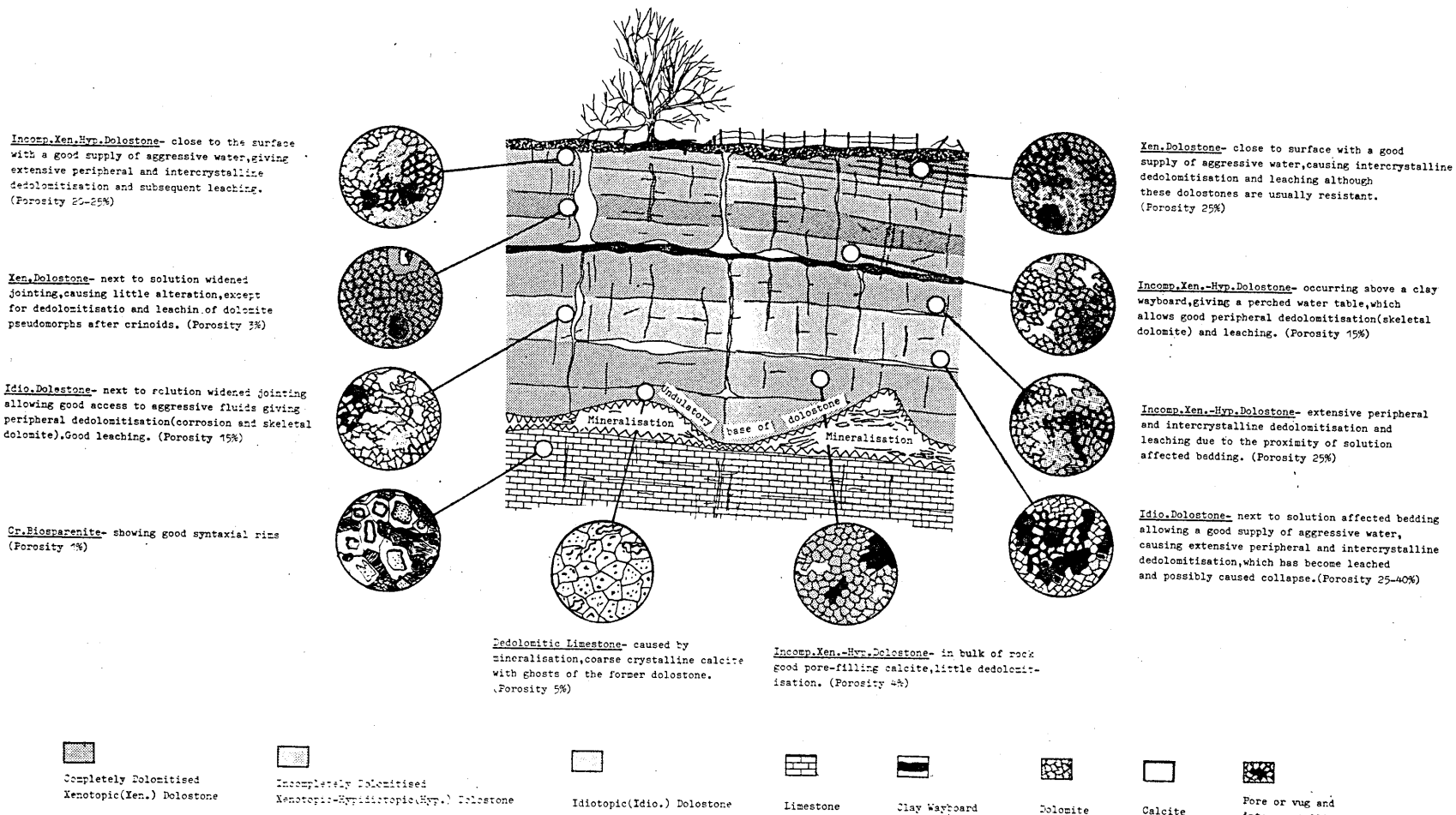


Figure 10 An idealised section through the dolostone succession of the Wirksworth area,showing the various zones of leaching dedolomitisation associated with karstification.

Leaching of this dedolomitisation calcite would lead to the disintegration of the rock and allow a dolomite sand to develop and the karst channel to widen. However, a completely dolomitised xenotopic dolostone contains little calcite and even adjacent to the channels develops little dedolomitisation or porosity.

In the Wirksworth dolostone most types of dolostone fabric can be found, thus allowing a range of dedolomitisation and porosity to develop, from the highly-porous idiotopic dolostones to the low porosity xenotopic dolostones (Section 5.3.1). Variation of both dedolomitisation and porosity may occur even within the same bed, due to variations in the original limestone fabrics. This allows the development of xenotopic and hypidiotopic dolostones in the same bed of dolostones, allowing significant local variation in dolostone weathering. This mixture of dolostone types also allows xenotopic dolostones, in favourable circumstances, such as at the surface, to be extensively dolomitised. Calcium-charged waters from the calcite-rich hypidiotopic dolostone penetrate the xenotopic dolostone, causing intercrystalline dedolomitisation (pl. 31b). A similar feature may be found associated in the xenotopic matrices of incompletely dolomitised hypidiotopic and idiotopic dolostones, adjacent to calcite-filled pores.

In the main bulk of the dolostone away from the influence of joints, bedding, etc., dedolomitisation

and leaching is limited. Yet the dolostones develop a variable, though quite high (av. 8%), porosity, indicating that leaching in the vadose zone may be occurring more quickly than dedolomitisation. This suggests that dedolomitisation will never completely destroy a formation, where insufficient calcite is available to cause extensive dedolomitisation.

The discussion has centred upon the development of dedolomitisation around the polyhedral pores, however, a significant contribution towards the porosity of the dolostones is given by the dedolomitisation and leaching of the crinoidal pseudomorphs. It has been shown that dedolomitised crinoidal pseudomorphs correlate positively with the presence of calcite-filled polyhedral pores. In the areas of active dedolomitisation the saturated solutions will cause dedolomitisation of the dolomicritised crinoidal pseudomorphs. Dedolomitisation and leaching of these pseudomorphs can often be found where little dedolomitisation of the pores exists, which must reflect the greater reactivity of the dolomicrite. This may explain the abundant mouldic vugs occurring in almost completely dolomitised xenotopic dolostone, although only limited calcite is available. These crinoidal vugs, geochemically, present a problem and may have originated partly in the phreatic zone, allowing stabilisation of the dedolomitisation calcite to low-magnesium calcite. However, the relatively enhanced

porosities of the face of Harborough Rocks (Section 5.3.4) and the numerous samples showing mouldic vugs and calcite-filled vugs, suggests a more soluble nature to the calcite caused by dedolomitisation, and points once again to a recent vadose origin.

It has been mentioned that the only totally dedolomitised dolostones in the area are those associated with the numerous mineral veins (Section 4.4.5), which can be seen at Manystones and High Peak Quarries. The former dolomite textures within the dedolomitic limestone are shown by small inclusions (pl. 21f). These are enclosed within a coarsely sparry matrix only rarely showing any dolomite remnants. Faust (1949) has shown that in contact metamorphism, heating of dolomite will cause its dissociation into calcium carbonate and magnesium oxide. In a solution charged with carbon dioxide, which may be expected in this mineralisation due to its richness in calcite as a gangue mineral, the magnesium oxide will dissolve to the more soluble magnesium carbonate and be removed. The pervasiveness of the dedolomitisation and retention of ghosts clearly distinguishes this type from the meteoric dedolomitisation. Geochemically the dedolomitisation associated with the mineralisation consists of a low-magnesium calcite in contrast to the high-magnesium nature found during microprobe analysis of the meteoric dedolomitisation. This reflects either the mode of dedolomitisation which was able to effectively remove excess Mg^{2+} to allow deposition

of low-magnesium calcite, or the stabilisation of a former high-magnesium calcite under later phreatic conditions (Longman 1980).

In conclusion, it is believed that the dedolomitisation found in the study area does not represent alteration in saturated groundwater charged with sulphate ions. It is felt that if that had been the case it would have caused a more pervasive dedolomitisation, such as that described by Shearman et al. (1961) and Evamy (1967) and does not explain the localised nature of the dedolomitisation found in the dolostones of the Wirksworth area. Aggressive waters in the vadose zone, and to a limited extent in the phreatic zone, are believed to be the agents of dedolomitisation. These waters gain access to the formation via various karst channels, such as jointing bedding, stylolites and fractures, and cause dedolomitisation mainly around polyhedral pores. Where the supply of aggressive water is greatest, i.e. next to the various karst channels, extensive dedolomitisation and subsequent leaching may occur. The extent of this alteration will depend heavily upon the fabric of the dolostone present. The enhanced susceptibility of dolomicritised crinoidal pseudomorphs to dolomitisation, causes widespread dedolomitisation and often leaching, even within almost completely dolomitised xenotopic dolostones.

Plate 27 Dolomitisation(rusty colour) occurring around stylolites (arrow),Cross Quarry.Mendips.

4.4.6. Stylolitisation

Examples of stylolites can be found in the dolostones, but show no evidence of pressure dissolution and are believed to have been inherited from the former limestone (Section 3.2.3). The stylolitisation probably played an important role in the dolomitisation process, providing access for magnesium-rich fluids (pl. 27). Under present-day weathering their roles have been reversed and dedolomitisation can be shown to be occurring along many stylolites.

4.4.7. Veining

A number of samples can be seen to be transected by thin calcite veining. These have typical cavity-fill textures and formed contemporaneously with the pore-filling calcite and represent small fractures. Dedolomitisation can be found associated with these veins due to the presence of the calcite.

4.4.8. Silicification

Silicification is mainly confined to the fabric of the rock with few cherty beds being present. The silica seems to be restricted to the polyhedral pores, seemingly replacing the pore-filling calcite, although isolated quartz euhedra do occur in the dolomite matrix. The preferential silicification of the brachiopod fragments noted in the equivalent limestones can also be seen and could either be pre- or post-dolomitisation. The source of silica is assumed to be similar to that discussed in section 3.2.9.

CHAPTER FIVE

5. The Origin and Evolution of Porosity in the Dolostone

The economic importance of dolostones as providers of good porosities has already been discussed in Chapter I. Many workers have discussed the role which karstification plays in the enhancement of porosities (Howard 1928, Howard and David 1936, Hohlt 1948, Imbt and Ellison 1946, Thomas and Glaister 1960, Harbaugh 1967, Choquette and Pray 1970 and Steiglitz 1975), but few have discussed how this process operates in detail. Today the dolostones of the Wirksworth area are undergoing sub-aerial weathering, although the pore systems recognised represent a culmination of several phases of karstification. The study of this dolostone was possible due to numerous quarries, railway cuttings and boreholes drilled in the area.

The porosity of the dolostones has developed through many stages, from the high porosities of the lime muds and sand, to the low porosity limestones due to early diagenesis. From a brief period the porosity increased due to dolomitisation, although became occluded by a cavity-fill cement (possibly occurring after an intra-Carboniferous karst phase). Finally sub-aerial weathering has led to quite high porosities due to dedolomitisation and leaching. The complex evolution of the carbonate formation may have involved exposure of the dolostone during as earlier period (Ford 1964) and many features seen today may be related to this stage. A study of the

geochemistry of these rocks suggests, at least in part, that dedolomitisation and leaching occur today.

5.1 Porosity in the parent limestone

The many good quarry sections found beyond the dolostone outcrop (Middle Peak, Intake and Hoptonwood Quarries) allow recognition of the different limestone types (Appendix I). The porosities of these limestones range between 1 and 10 percent but in general are quite low (Table VII). This contrasts very markedly with the depositional porosities of the present-day lime muds and sands. This primary porosity, probably of the order of 60 - 70 percent, has been destroyed, during diagenesis, as a result of primary cementation, pressure solution, neomorphism and cementation by a low-magnesium cavity-fill cement (Chapter III).

Sample No.	Porosity %	Limestone Type
HW26	2.41	Br. Biomicarenite
IQ16	5.45	Br. Biomicrosparenite
L_2 7	1.54	Br. Biomicrosparenite
L_4 5	2.60	Br.-Al. Biomicarenite
L_6 2	1.75	Biomicarenite
1A	1.30	Biomicarenite
2A	0.99	Cr. Biomirosparenite
5A	1.19	Br.-Cr. Biomicarenite
L_1 6	4.76	Cr. Biomicarenite
3A	1.39	Cr. Biomicarenite
HW1	10.80	Cr.-Al. Biosparenite
HW8	7.69	Cr.-Al. Biosparenite
3B	0.99	Biosparenite
4B	1.12	Biosparenite
6C	2.44	Cr. Biosparenite
8A	1.47	Cr. Pelsparenite
8B	3.33	Foss. Pelsparenite

Table VII Limestone porosities

Table VII indicates the range of limestone types in the area and their porosities, and shows that distinct ranges of these porosities exist for the micarenites and sparenites.

The micarenites represent former lime muds with varying amounts of allochems (mainly biological) which have become indurated due to neomorphism and cavity-fill cementation. These show only 1 - 5 percent intercrystalline

porosity, more commonly showing little more than 2 percent. The slightly higher porosities are mainly due to a small amount of intraparticle porosity. The porosity is disseminated throughout the finely crystalline micrite as small intercrystalline pores (1μm) between equant calcite crystals (pl. 28a).

The sparenites represent fairly well-sorted fossil sands, in which the porosity became occluded by early cementation, pressure solution and, most significantly, cavity-fill cementation. These have a slightly higher range of porosity from 2 percent up to 10 percent but normally average 5 percent. The majority of the porosity, particularly in the slightly more porous samples is due to the failure of the cavity-fill cements to completely fill the inter-particle pores. The porosity is more localised, consisting of intercrystalline pores (500um - 1mm), scattered throughout the sample, which are easily identified in thin sections. Micritic material can also contribute to the fabric of the sparenites and thus more widespread intercrystalline porosity may be present.

Although the porosity in the sparenites is greater, the amount of surface area available for attack by dolomitising fluids is much less than in the micarenites. This is due to the crystal size and disseminated nature of the porosity in the micarenites. Thus, the micritic material allows greater access to the dolomitising fluids, causing a greater nucleation to give the xenotopic and

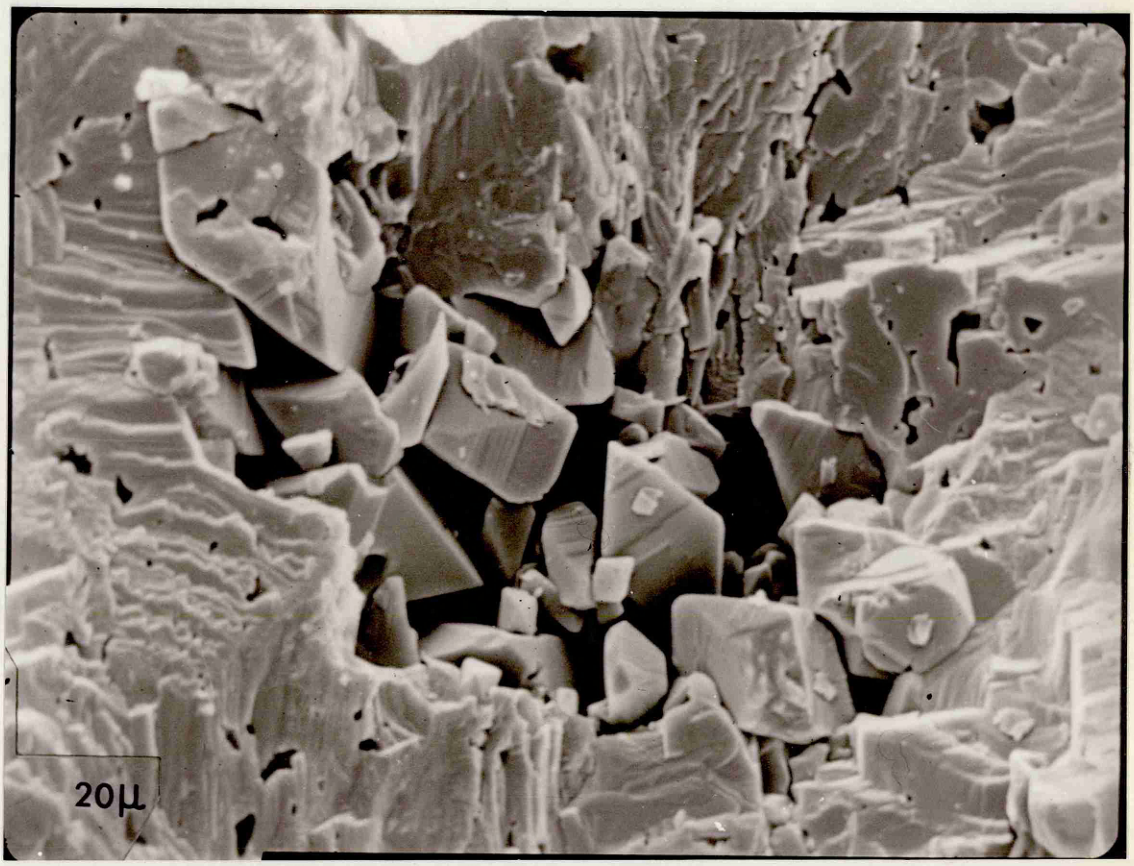


Plate 28 S.E.M. photographs of the limestone and dolostone porosity, (a) intercrystalline porosity of micrite,with equant calcite crystals. and (b) polyhedral pore in quite coarse dolomite, filled with small euhedral dolomite crystals.

hypidiotopic dolostones noted in Chapter IV. The sparenites allow only localised access, and thus form the less completely dolomitised hypidiotopic and idiotopic dolostone and dolomitic limestones.

Sub-aerial weathering has resulted in a karstification overprint upon the limestones as evidenced by caves and solution-widened jointing and bedding planes. The karstification is not necessarily a consequence of present-day weathering. It probably represents the culmination of a number of different phases of karstification. In the study area there are two examples of palaeokarstification (Section 6.2), one is that associated with the Late Triassic mineralisation (Ford 1967) and the other is represented by sand-filled sink holes eg. Bees Nest Pit, which is considered to be of Neogene age (Walsh et al. 1972). The development of karstic features is poor in the limestone sections exposed in the quarries, the most prominent feature being solution-widened joints (plate I). No significant enhancements of porosities in the micarenites and sparenites close to these features can be shown. The only significant porosity developed is that of the aforementioned karst features themselves. Sections were measured in the Matlock and Hoptonwood limestones in order to estimate this porosity. This was performed on a number of karstified quarry faces by measuring each individual solution-widened joint and bedding plane. The measured sections represent near-surface outcrops, and within the depth of the quarry (25 - 30m) widened joints can be shown to close downwards quite

considerably (pl. 1), thus further decreasing the importance of the karstic features. Bedding appears to contribute little to the karstic porosity due to the presence of clays occurring as impurities within the limestone or clay wayboards. An overall porosity of 1 - 2.5 percent is given, in agreement with similar measurements taken in South Wales and the Mendip Hills.

Karstification prior to dolomitisation may have had a significant influence upon the access of dolomitising fluids to the formation. Evidence for a pre-Namurian unconformity is found at Treak Cave, near Castleton (Ford 1964), to the north of the area, where swallow holes are filled by limestone boulders in a black shale matrix. The shale is typical of the lower Namurian. Some estimates of uplift above sea level are in excess of 500ft. for a period of perhaps a million years or so (Ford 1964) (Section 6.2).

5.2 The primary dolostone porosity

The process of dolomitisation has inevitably led to an increase in porosity, the extent and type of porosity developed depends largely upon the mode of dolomitisation. Murray (1960) summarised the two modes of dolomitisation outlined by many writers, (a) by a molecule for molecule, and (b) a volume for volume replacement. The first was originally hypothesised by Elie de Beauman in the 19th century and since endorsed by many writers, none more significant than Weyl (1960), whereby Mg^{2+} ions substitute for Ca^{2+} ions, the carbonate being supplied locally. The greater density of the magnesium will lead to 12 - 13 percent decrease in

volume in addition to the porosity of the original limestone. A volume for volume replacement suggested by Stiedtmann (1911) and confirmed by Lindgren (1912), Landes (1946) and Murray (1960), involves no decrease in volume, and thus excess carbonate material must be supplied along with the incoming magnesium ions. In this study, as suggested in Chapter IV, a volume for volume replacement is believed to have occurred giving a number of differing dolostone types.

The variety of dolostones developed during dolomitisation means that an equally variable range of porosities was able to develop, upon leaching of remnant calcite. The completely dolomitised xenotopic dolostones (Section 4.4.1(1)) show little more than porosity inherited from the original micritic limestones, which seldom exceeds 2 percent. The incompletely dolomitised xenotopic-hypidiotopic and idiotopic dolostones have porosities which range between 5 and 40 percent* due to the variation in the amount of resistant sparry material present and the accessibility of dolomitising brines. Originally the polyhedral pores (50 - 500um diameter and mouldic pores (300um - 10mm diameter) were infilled by a remnant calcite, which has since been leached (Section 4.4.1(2)). Leaching may have occurred at a number of intervals both during and after dolomitisation. Murray (1960) suggests that

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*Due to the cemented nature of these dolostones an estimate of the original porosity was given by a simple point-counting technique of the cavity-fill cement.

leaching of this remnant calcite may occur during the latter stages of dolomitisation, supplying carbonate ions to the waning dolomitisation. Alternately leaching occurred during one of the many periods of sub-aerial weathering noted by Ford (1964) and discussed in Chapter VI. Porosity in the partially dolomitised limestones was inherited from the parent limestone. The undolomitised calcite in these limestones, when abundant, can cause an inhibition of differential leaching. For example, the ease of access of fluids to the more completely dolomitised dolostones, together with the more localised occurrence of calcite allows differential leaching. Where the calcite is abundant and the dolomite consists of isolated crystals, fluid access would have been poor and differential solution negligible, thus dolomitic limestone weathers rather like limestone. This produces little internal porosity, as seen in the more completely dolomitised hypidiotopic dolostone. The more sporadic occurrence of calcite in these dolostones allows differential dissolution of calcite, gradually allowing greater internal access and consequently greater internal dissolution.

Murray suggested that "dissolution appears to be restricted to those dolostones which had already attained a high degree (50 percent) of disseminated dolomitisation". A more realistic figure, though not experimentally proven, seems to be between 60 and 70 percent, and may be supported by Murray's figure 10 (1960). Therefore an upper limit for the development of primary porosity in the Wirksworth dolostone, prior to occlusion by late pore-filling calcite, would appear

to be between 30 and 40 percent, although 25 percent is the highest primary porosity found. The extent of the primary porosity in these dolostones, due to selective dolomitisation, is dependent upon the original fabric of the limestone. This gives a range of porosities from 5 up to 25 percent. It has been shown that the parent limestones have various fabrics and thus develop variable dolostone types and a number of different porosities.

In the Wirksworth area today, primary porosity in the dolostones has been destroyed or modified. Some of the primary dolostone porosity has become occluded by the later outer zoning of the dolomites and small euhedral crystals (pl. 28b). The low porosities seen throughout much of the dolostone succession is due to cavity-fill calcite cement which has reduced the original high porosities to less than 2 percent. It is impossible to date exactly the time of cementation which could be related to any one of the four known periods of sub-aerial exposure noted by Ford (1964), since the dolomitisation of the limestone.

Many dolostones show quite high porosity at the weathering surface as well as at depth. Some samples seem to show a regeneration of primary porosity, although modification and enhancement due to dedolomitisation is common (Section 4.4.5).

5.3 Karstification and its role in the development of secondary porosity

Karstification has been found to have an importance in the development of dolostone porosity, by many writers

(Howard 1928, Howard and David 1936, Imbt and Ellison 1946, Hohlt 1948, Thomas and Glaister 1960, Harbaugh 1967, Choquette and Pray 1970 and Steiglitz 1975). What follows is a brief account of the factors controlling the dissolution of carbonates to give the characteristic karst features. The account is far from exhaustive and for greater detail the reader is referred to the references mentioned in the text.

The percolation of water through soluble rock and its circulation underground is the essence of the karst process - a process which is dominated by dissolution. Cvijic (1893) was the first to write a comprehensive treatise on karst landforms. He described many of the features we associate with karstification today, such as caves, swallow holes ("ponors" of Cvijic), dolines (closed hollows), karren (linear features eg. grikes) and poljes (flat cultivated areas), indeed Cvijic was the first to discuss the origin of these features in relation to solution. Since this time many papers have appeared dealing with every aspect of karstification, most noteworthy are those of Davis (1930), Swinnerton (1932), Bretz 1942), Trombe (1952), Warwick (1962) and Sweeting (1972).

A number of carbonate minerals are found in common carbonate rocks, the more common being calcite, dolomite and aragonite. These react to the different factors controlling the dissolution in similar ways, except that the solubilities differ slightly. Thus, for simplicity, only the dissolution of calcite will be discussed in detail.

Smith and Mead (1962) mention that calcite dissolves in gas-free water to give 12p.p.m. of calcium carbonate in solution at 10°C. There is a great discrepancy between this figure and data recorded from natural carbonate waters, which are much higher. It has long been known that carbon dioxide dissolves in water to form carbonic acid, it is an important factor in dissolution. The full reaction is as follows:-

$$CaCO_3 + CO_2 + H_2O = Ca(HCO_3)_2$$

A summary of the equilibria involved is as follows:-

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \quad \text{(Eqn. (1))}$$

Calcium carbonate is slightly soluble and in solution will dissociate to give calcium and carbonate ions:

$$CO_2 + H_2O = CO_2(aq.) + H_2O \quad \text{(Eqn. (2))}$$

$$CO_2(aq.) + H_2O = H^+ + HCO_3^- \quad \text{(Eqn. (3))}$$

When carbon dioxide dissolves in water to form carbonic acid it produces H^+ ions (eqn. 3) which combine with the carbonate ions of calcite dissolution (eqn. 1), to give bicarbonate. To maintain its equilibrium more calcium carbonate dissociates:

(1) $CaCO_3 = Ca^{2+} + CO_3^{2-} = HCO_3^-$

(2) $CO_2(aq.) + H_2O = HCO_3^- + H^+$

Thus, assuming that the supply of carbon dioxide remains constant, the dissociation of calcite will continue until an equilibrium is reached, then the solution is considered to be saturated with respect to calcium carbonate. If the solution has not reached equilibrium it is undersaturated and is termed aggressive. A decrease in the carbon dioxide

would mean a movement of the reaction to the left and calcium carbonate would precipitate.

A rise in the carbon dioxide content of the solution would increase its aggressivity and allow more calcium carbonate to dissolve. The volume of carbon dioxide dissolved in water is proportional to its pressure above the water, if the temperature remains constant (Henry's Law). However, the atmosphere is a mixture of gases which include carbon dioxide. The amount of gas dissolved will depend upon its partial pressure (Dalton's Law). When considering carbon dioxide it must be remembered that it reacts with water to form carbonic acid, thus causing the carbon dioxide content of the water to fall and so more dissolves (eqns. 2 and 3).

In the atmosphere, carbon dioxide has a partial pressure of 0.0003 atms.. Rainwater passing through the atmosphere and absorbing carbon dioxide would be capable of dissolving 74 p.p.m. calcium carbonate at 10°C under "equilibrium conditions" i.e. where water is constantly in contact with air and able to attain eqiulibrium. On the other hand, under anaerobic conditions (i.e. where the air supply is cut off and thus the carbon dioxide levels are not constantly regenerated), after attaining initial equilibrium, rainwater would only be capable of dissolving 14 p.p.m. calcium carbonate, see figure 11 (Smith and Mead 1962).

Such levels are again far below that found in natural carbonate waters, and Adams and Swinnerton (1937) were really

the first to draw attention to soil as a major supplier of carbon dioxide, when considering the dissolution of calcite. Russell (1950) gave a figure of 1 - 6 percent carbon dioxide present in a soil under a grassland cover, which is some fifty times greater than the atmosphere. This may explain the higher concentration of carbonate found in natural waters. Smith and Mead (1962), who although accepting that soil carbon dioxide was a significant source, still had reservations concerning it being the absolute source of carbon dioxide. Tratman (1957) and Atkinson (1977) contend that groundwater atmosphere of the vadose zone is a further source of carbon dioxide, due to the decay of plant material falling from the surface, into the vadose zone.

Temperature has been found to have a profound effect upon the solubility of carbon dioxide and consequently upon the solubility of calcite. Chantry (1949) gives the following figures:-

Temp. in ^{o}celsian	0	5	10	15	20
CO_2 gm/cc	1.014	0.836	0.705	0.601	0.504

This is because of the equilibria involved during the dissolution process, which are temperature dependant. Thus it might be expected that solution would be greater in colder climates (Corbel 1957), instead it has been found that solution, if anything, is greater in warmer climates. (Sweeting 1972, Brown and Ford 1973, Drake and Wigley 1976). This is probably due to greater biogenic activity in the

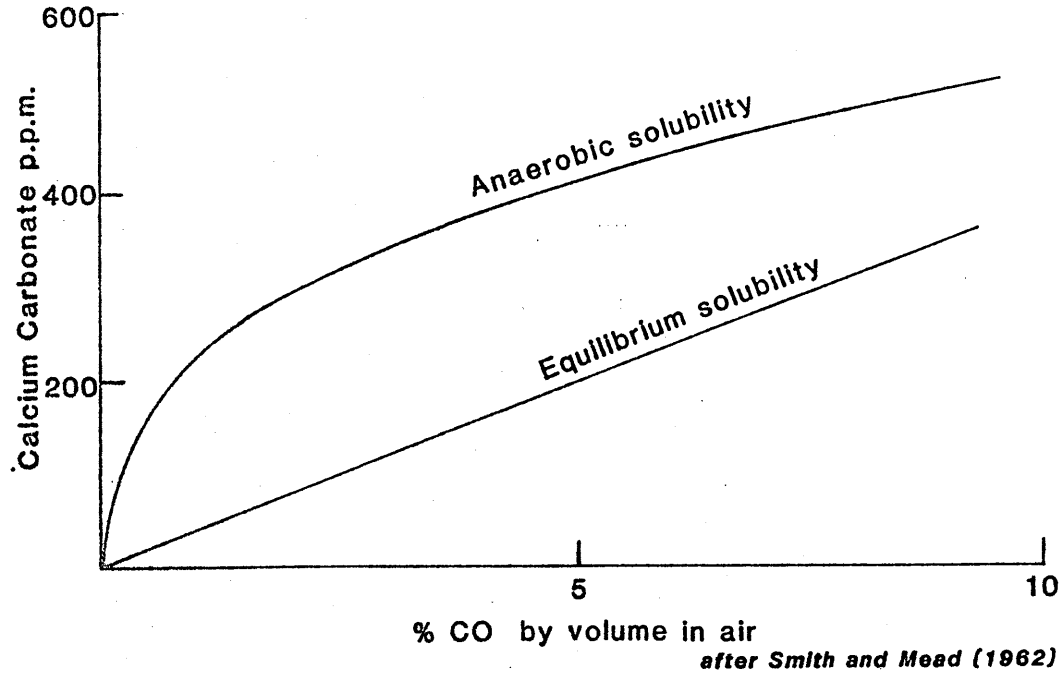


Figure 11 Dissolution curves of calcite under equilibrium(aerobic) and anaerobic conditions.

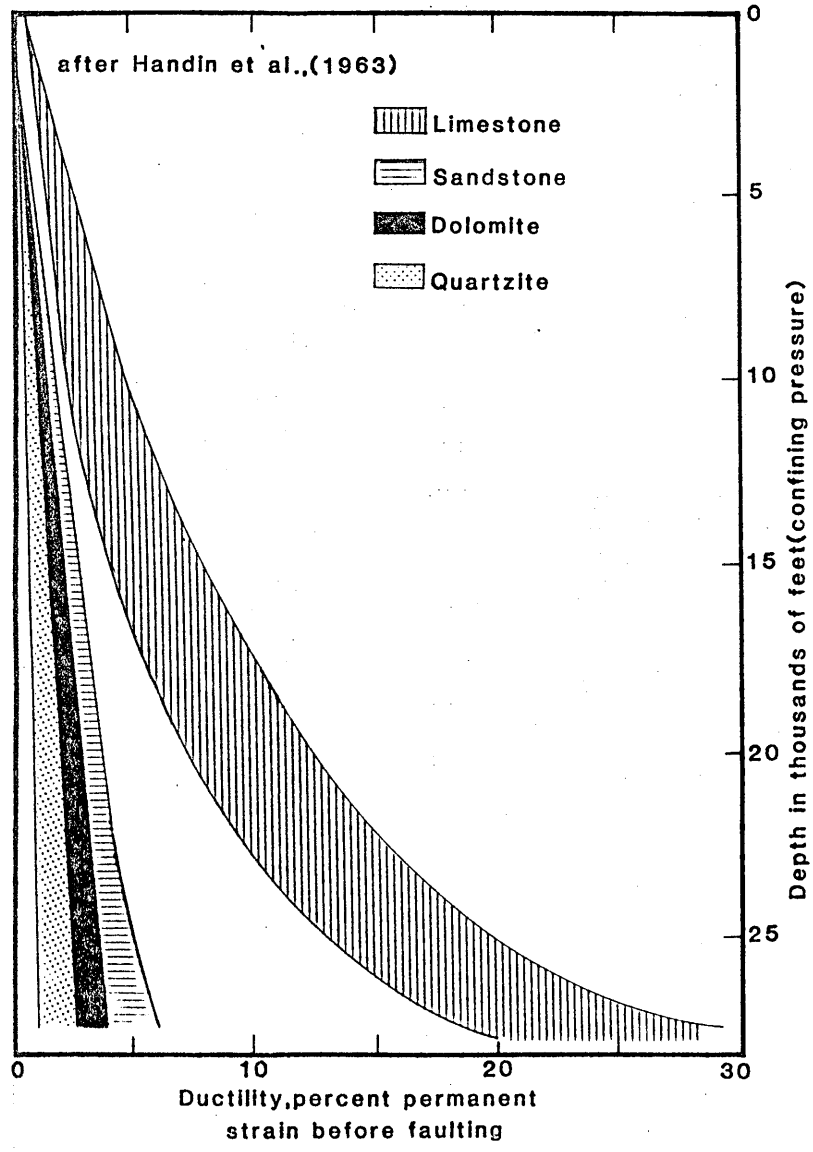


Figure 12 A plot of ductility versus depth, indicating that dolostones are less ductile particularly at greater depths and thus more prone to fracture.

soils at higher temperatures and thus the greater carbon dioxide content of the soil may offset the expected decrease in calcite solubility (Drake and Wigley 1976), if we presume rainfall to be equal. Seasonal changes of temperature and associated increase in biogenic activity would thus be expected. There are examples of rising calcium carbonate content with increasing temperature eg. Poole Cavern, Peak District (Pitty 1971), the River Mellte, South Wales (Groom and Williams 1965) and Bruce Peninsula, Ontario (Cowell and Ford 1980). Malham Tarn, however, shows the opposite trend, but this is due to apparent decrease of calcium carbonate in solution, due to the abundance of lime-secreting algae.

The dissolution of calcite depends heavily upon the presence of acids, mainly carbonic acid. Other acids can be found associated with carbonate. Humic and inorganic acids, such as sulphuric acid formed by the oxidation of sulphide mineralisation so commonly associated with carbonate rocks, may all play a small but significant part in the dissolution process.

Bamber (1952) and Tratman (1957) believe that turbulence can increase the solubility of calcium carbonate. However, increased turbulence could cause degassing of solution and calcium carbonate would be deposited rather than dissolved. Any increased solubility due to the turbulence is probably by corrasion. The turbulence and velocity of water passing through a carbonate would have a greater effect upon the rate of solution, and is probably the most important factor

in determining the rate of solution for any given level of aggressivity. Other factors affecting the rate of solution are the rate of the reactions involving: (1) dissociation of calcite to give Ca^{2+} and CO_3^{2-}, (2) reaction between CO_3^{2-} ions and dissolved carbon dioxide, (3) the solution of carbon dioxide in water and (4) the rate of transport of ionic species into solution. Graf and Lamar (1950), Kaye (1957), Plummer et al. (1978) and Berner (1978) discuss these factors.

Picknett (1964) found that trace amounts of certain elements, such as lead, zinc, copper, manganese, scandium and lanthanum can drastically alter the solubility of calcium and magnesium carbonate. For example, 0.2 percent scandium can reduce the solubility of calcite by half. On the other hand, Akin and Lagerwerff (1965) found that the presence of magnesium and sulphate ions enhances the solubility of calcite.

Having discussed the factors which influence the process by which calcite can be dissolved, we turn next to study the effect which physical characteristics eg. the mineralogy, porosity, fabric, stylolites, bedding, unconformities, jointing and faulting may have upon the dissolution of carbonates.

Naturally occurring carbonate rocks are mainly composed of the three most common carbonate minerals, namely calcite, dolomite and aragonite. Aragonite more commonly occurs in modern sediments, and does not concern us in this study.

Dolomite is much more abundant in ancient carbonate formations, being less soluble than calcite (Clarke 1924, Garrels et al. 1960 and Schoeller 1962). The solubility of dolomite under sub-aerial conditions was noted earlier.

Porosity has a significant influence upon the dissolution process because the greater the porosity, the greater the surface area available for attack. This is particularly important in dolostones, which tend to have greater porosities. Although limestones generally have lower porosities, particularly finely crystalline micritic and coarser sparry limestones, some biomicrites such as those noted by Sweeting (1972) in N. W. Yorkshire have higher porosities, and evidence suggests greater dissolution of the biomicrites than the highly crystalline sparry limestones, weathering under similar conditions. Ollier and Tratman (1956) also suggested that calcite spar is less soluble than finer grained calcite. However, the work of High (1970), and the results of his research, show no significant positive correlation between fabric and solubility.

Fractures such as joints and faults form a very important part of any groundwater circulation, especially in karstified formations where they are the principal means by which these waters obtain access to the formation. It has been shown that under certain conditions dolostones are stronger and more brittle than limestone (figure 12) and tend to form many more fractures when stressed (Handin and Friedman 1955, Handin et al. 1963, Stearn 1967, Stearn and

Friedman 1972). These studies, however, ignore the considerable variation of fabric in carbonate rocks. Doughty (1968), Stearns and Friedman (1972) and Sweeting (1972) mention that joint density does seem to vary with fabric: dolostones and finely-crystalline limestones seemingly have many more fractures than coarsely-crystalline limestones. Donath (1968) and Hugman and Friedman (1979) studied the effect which different fabrics have upon the strength of carbonates. They found that micritic material is more brittle and that the ultimate strength is proportional to the content of microcrystalline and dolomitic material. The differing strengths of dolostones again depend upon their fabric, more coarsely crystalline anhedral dolostones are weaker than euhedral and microcrystalline ones (Hugman and Friedman 1979).

Bedding, unconformities and stylolites must have had an effect upon the initiation of channelways into a carbonate formation. Bedding planes are of great significance in the formation of caves, as shown by the abundance of bedding caves. These features are frequently associated with changes in lithology. Shale, although insoluble, can form an important impermeable barrier. Under sufficient pressure water percolates through the shale, causing oxidation of pyrite to produce sulphuric acid which causes leaching of carbonates. A good summary of the features that contribute to the formation of a well-karstified formation have been outlined by Ford (1971).

The development of the porosity in the dolostones of this study due to sub-aerial weathering, was studied in two

ways: firstly, by surface traverses to compare relative porosities of comparable limestones and dolostones, and secondly by boreholes to study the stratigraphical variation (figure 13) at depth.

5.3.1. Traverses across the limestone - dolostone transition

Ten traverses across the limestone/dolostone boundary were sampled (figure 13), to study (a) the variation in porosities across the boundary and (b) the development of secondary porosity caused by surface weathering.

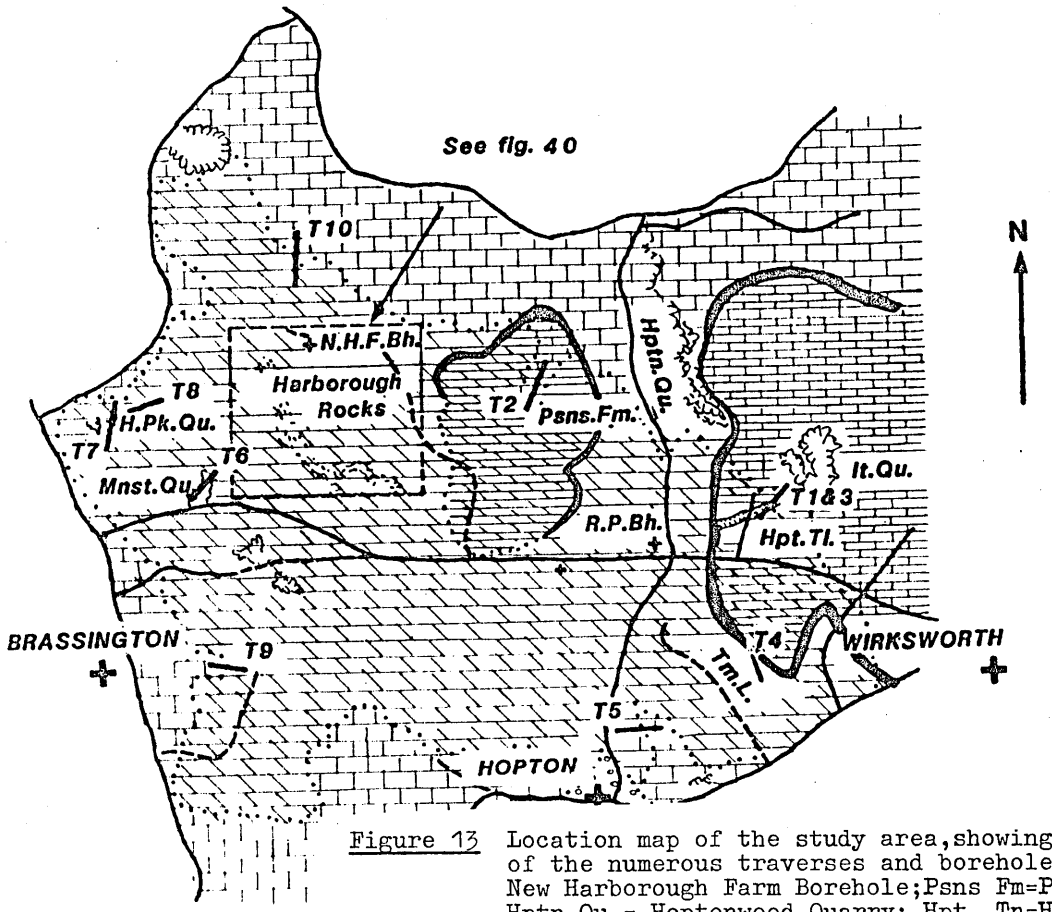


Figure 13 Location map of the study area, showing the position of the numerous traverses and boreholes. N,H.F.Bh.= New Harborough Farm Borehole; Psns Fm=Pearson's Farm Hptn Qu.= Hoptonwood Quarry; Hpt. Tn=Hopton Tunnel Tm. L.=Tiremare Lane It. Qu.= Intake Quarry; H.Pk.Qu. = High Peak Quarry; Mnst. Qu.= Manystones Quarry; R.P.Bh. = Ryder Point Borehole

Figures 14 to 23 show the porosity and CaO/MgO ratio profiles for the traverses. Porosity of core and chipped samples was calculated using a simple wet and dry technique (see Appendix IV). The CaO/MgO ratio, determined by E.D. X-r-f (see Appendix VI), indicates the degree of free calcite present

in the dolostone, assuming an ideal dolomite CaO/MgO of 1.391. X.r.f. analysis was supplemented by a detailed petrographic study of each sample using Alizarin Red-S stained thin sections.

(a) Traverse 1 and 2 (figures 14 and 15)

Traverse 1 is a vertical section 10 centimetres long across the limestone boundary in the Matlock "Group", exposed in the cutting to the east of Hopton Tunnel (figure 13) (Ref. 266548).

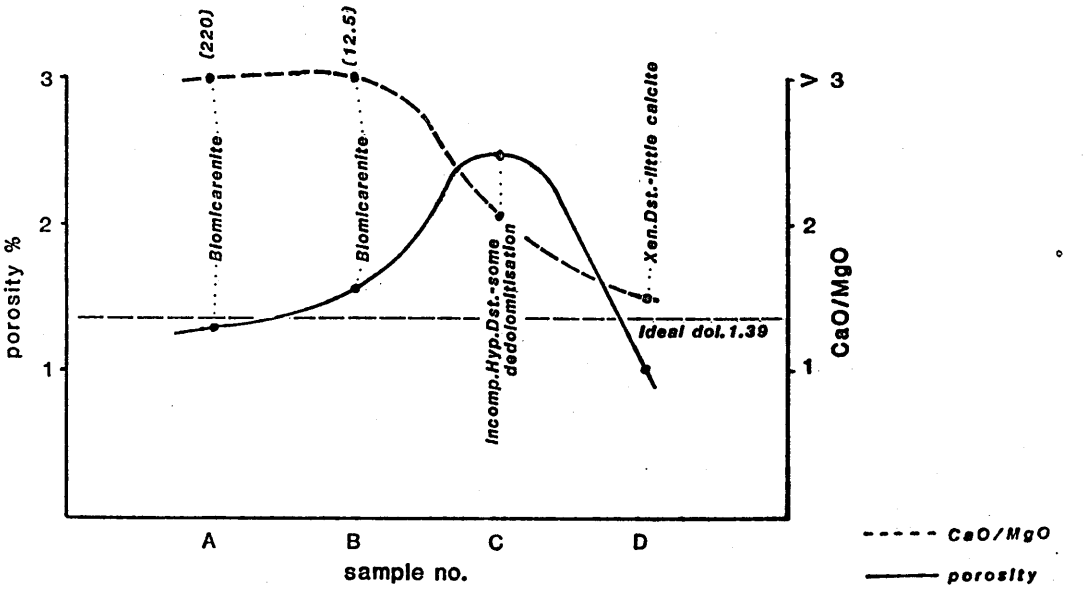


Figure 14 Plot of the CaO/MgO ratios and porosity values across the limestone-dolostone transition at Hopton Tunnel- Traverse 1.

Traverse 2, however is a horizontal ground transect, 3 metres long, across the limestone-dolostone boundary in the Hoptonwood "Group", exposed to the north-west of Pearson's farm (figure 13) (Ref. 260557). The traverses are grouped together because of similarities in their lithologies and porosities.

The transformation of biomicarenite (samples 1A and 1B) into xenotopic dolostone (sample 1D) has resulted in a decrease in porosity. The CaO/MgO ratio decreases in accordance with the petrography (Section 4.4.1), the xenotopic dolostone having only a slightly higher CaO/MgO than pure dolostone, indicating little free calcite.

Thin sections of the dolostone show an interlocking anhedral dolomite, indicating volume for volume replacement, the porosity of the dolostone being inherited from the original limestone. Sample 1C does not conform to this simple trend in that it has higher CaO/MgO ratio and porosity than the xenotopic dolostone (sample 1D). The higher CaO/MgO ratio is due to incomplete dolomitisation giving excess calcite (Section 4.4.1(2)). The lack of complete dolomitisation is believed to be a consequence of dwindling dolomitising fluids during the later stages of dolomitisation. Leaching of the calcite during recent times has given rise to the slightly higher porosity. The porosity has not developed to any significant extent, due to the presence of xenotopic dolostones above, which tend to be impermeable and give a reasonable protection from percolating groundwater.

In Traverse 2, the biomicarenites have become totally replaced by a finely-crystalline xenotopic dolostone (figure 15) with only a slight increase in porosity.

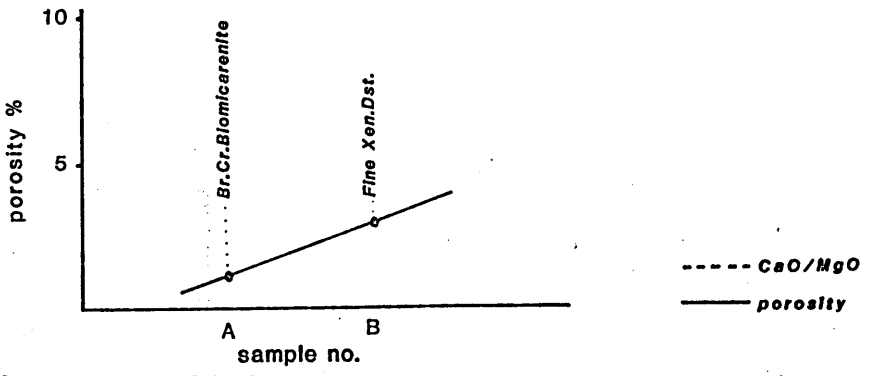


Figure 15 Plot of the CaO/MgO ratios and porosity values across the limestone-dolostone transition just north of Pearson's Farm-Traverse 2

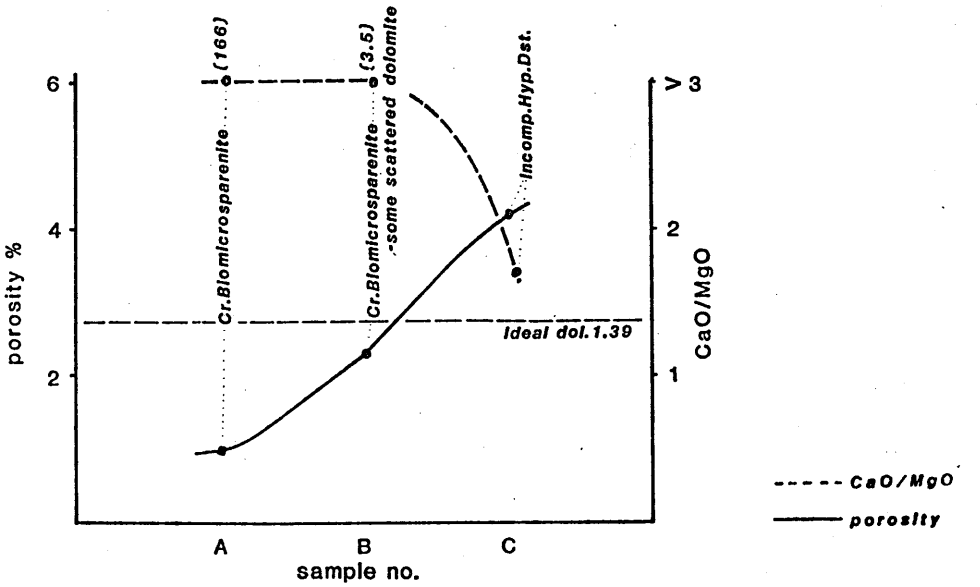


Figure 16 Plot of the CaO/MgO ratios and porosity values across the limestone-dolostone transition at Hopton Tunnel-Traverse 3

(b) Traverse 3 (figure 16)

The traverse is a vertical section, 10 centimetres long, across the limestone-dolostone boundary in the Matlock "Group" exposed in the cutting to the east of Hopton Tunnel. The crinoidal biomicrosparenites (samples 3A and 3B) have low porosities around 1 percent, due to their well-cemented nature. Abundant micrite is found associated with the microspar and gives rise to the localised development of xenotopic dolomite. Dolomitisation has led to an almost completely dolomitised xenotopic-hypidiotopic dolostone (sample 3C) with rare calcite-filled pores (figure 16), consequently leaching has not been able to enhance the porosity to more than 3 percent.

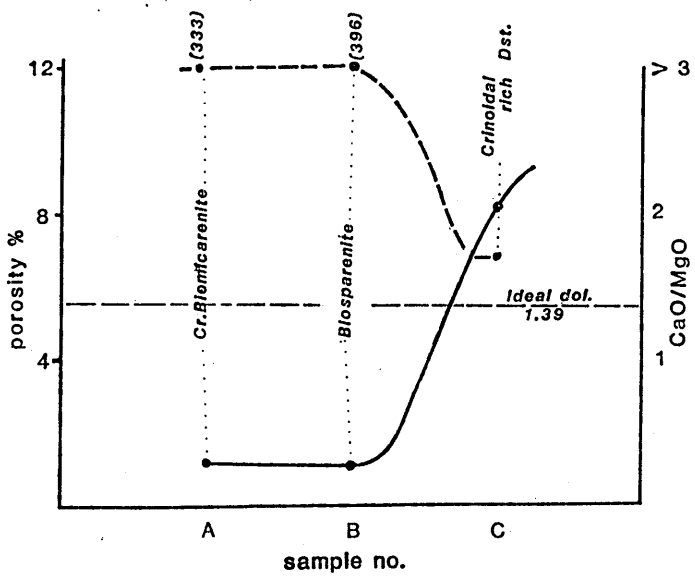


Figure 17 Plot of the CaO/MgO ratios and porosity values across the limestone-dolostone transition just east of Tiremare Lane -Traverse 4

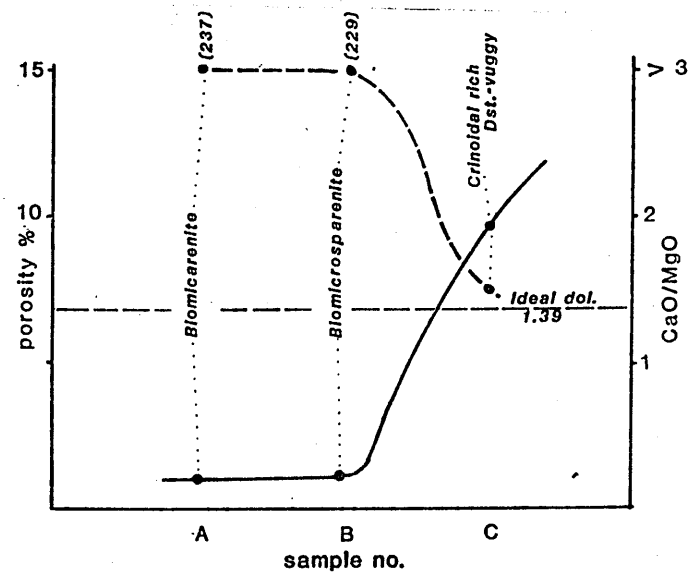


Figure 18 Plot of the CaO/MgO ratios and porosity values across the limestone-dolostone transition just north of Hopton village -Traverse 5

Sample 3B, an incompletely dolomitised crinoidal limestone, gives intermediate porosity and CaO/MgO values, and is a consequence of its marginal nature and dwindling supply of dolomitising fluids (Section 4.4.1(2)). A thin section of this sample shows a dolomitisation front (Section 4.4.1(5)), ahead of which only selective replacement of calcite by dolomite has occurred (pl. 19b). This mixture of dolostone and dolomitic limestone gives a higher porosity and CaO/MgO ratio, in a similar manner to Traverse 1. In both traverses the small amount of clacite has allowed little dedolomitisation or leaching and consequently no enhanced porosities have developed.

(c) Traverses 4 and 5 (figures 17 and 18)

The traverses are both horizontal ground sections, approximately 5 metres long, across the limestone-dolostone boundary in the Hoptonwood "Group". Traverse 4 was sampled just north of the Tiremare Lane (figure 13) (Ref. 265538), where a small enclave of limestone occurs, remaining unaltered due to the protective nature of the overlying Lower Matlock Lava (Section 2.1(2)). Traverse 5 was sampled 1 km. west of 4, just to the north of Hopton village (figure 13) (Ref. 258534).

Both these traverses show very similar porosity and CaO/MgO profiles and the dolostone samples 4C and 5C have very similar petrographies. The biomicarenites (samples 4A and 5A) have varying amounts of crinoidal material and have become almost totally dolomitised to give a xenotopic dolostone (see figure 6) with numerous large anhedral dolomite pseudomorphs after crinoids. The CaO/MgO ratio, although slightly higher in Traverse 4, indicates little free calcite, yet the samples 4C and 5C have quite high porosities. Petrographically the samples show little free calcite and intercrystalline pores are rare. Dolomicritised crinoidal pseudomorphs can be seen but only slight evidence for dedolomitisation calcite was found, in spite of the fact that mouldic vugs are present. The slightly higher CaO/MgO ratio of Traverse 4 may indicate dedolomitisation crinoidal pseudomorphs, which must be the reason for the higher porosity. The greater solubility of these dedolomitised pseudomorphs (Section 4.4.5) has led to a greater leaching not only of the pseudomorphs,

but also of intercrystalline cements, due to the greater access for aggressive waters provided by the mouldic vugs.

(d) Traverse 6 (figure 19)

This traverse is a metre long vertical section in the Hoptonwood "Group" and was sampled at Manystones Quarry (Ref. 236552).

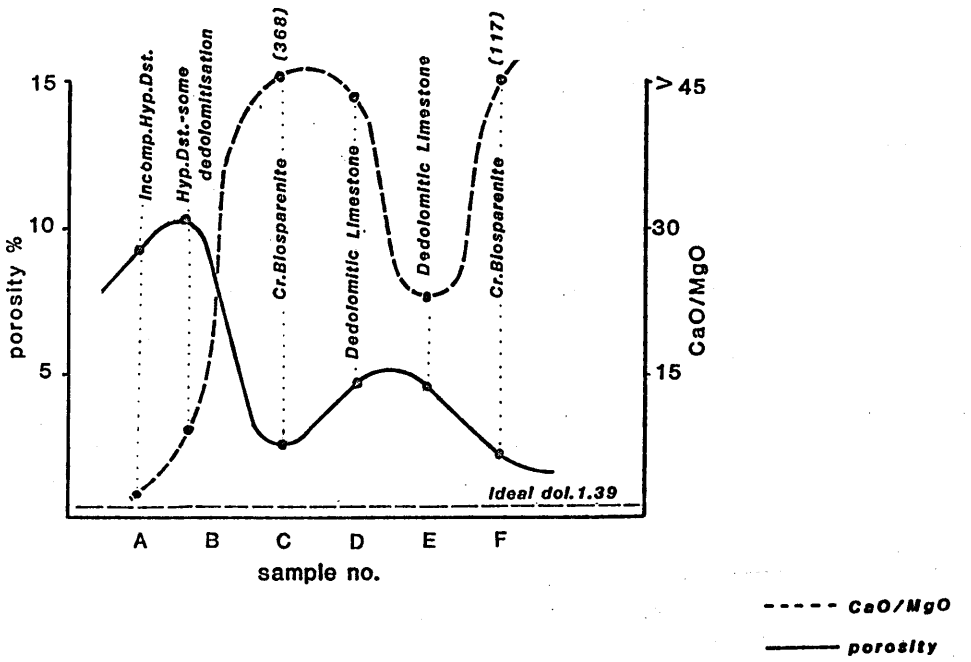


Figure 19 Plot of the CaO/MgO ratios and porosity values across the limestone-dolostone transition at Manystones Quarry-Traverse 6

Here the limestone-dolostone boundary is marked by the presence of caves which have been partially infilled by lead-zinc mineralisation (Section 6.2.). The mineralisation at this locality is marked by a coarsely crystalline calcite gangue.

Samples 6A and 6B represent a dolomitised crinoidal biosparenite (6C and 6F), giving an incompletely dolomitised xenotopic-hypidiotopic dolostone (figure 6). They show a good development of intercrystalline pores, due to the abundance of sparry material (after crinoidal fragments), hence the high CaO/MgO ratio (sample 6B). Surface weathering has caused leaching of the calcite to give quite high porosity to the dolostone. The porosity is simply a regeneration of a slightly modified primary dolostone porosity due to dedolomitisation which on leaching brings about an enhancement of the original porosity. Certainly the majority of the porosity is slightly modified primary dolostone porosity, but in other samples where dedolomitisation is very extensive leaching leads to porosities as high as 20 - 30 percent.

The traverse also shows a totally dedolomitised sample, with ghosts of former dolomite crystals (sample 6D). These were produced by the mineralisation (Section 4.4.5(1)), associated with the karstified limestone-dolostone boundary. The "dedolomitic limestones" show little, if any, increase in porosity from the original dolostone, prior to the leaching of the cavity-fill cement.

(e) Traverse 7 (figure 20)

Traverse 7 is a vertical transect, 5 metres long, across the limestone-dolostone boundary, which is again marked by kartification and mineralisation. It was sampled within the Hoptonwood "Group" at High Peak Quarry (figure 13) (Ref. 235558).

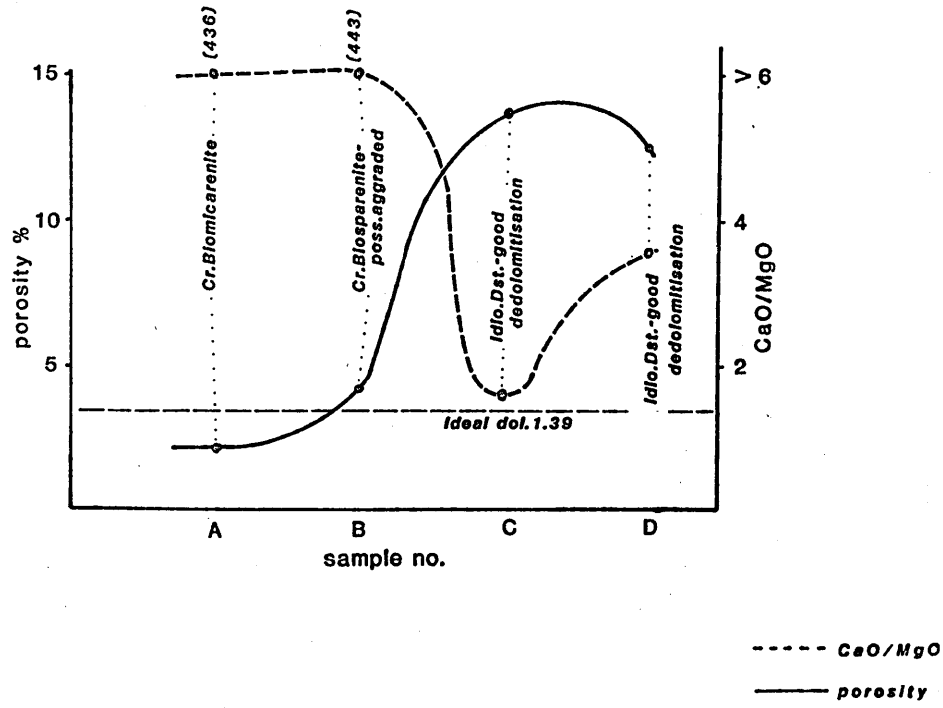


Figure 20 Plot of the CaO/MgO ratios and porosity values across the limestone-dolostone transition at High Peak Quarry-Traverse 7

The crinoidal-rich biomicarenites,(sample 7A) and sparenites (sample 7B), with their low porosities ranging between 2 and 8 percent, when dolomitised give hypidiotopic and idiotopic dolostones (figure 6). The CaO/MgO ratio indicates the extent of free calcite present (sample 7D), due to the incomplete dolomitisation of sparry calcite. Sub-aerial weathering and the presence of calcite led to widespread dedolomitisation and leaching to give quite high porosities, ranging between 12 and 15 percent. The CaO/MgO ratio shown by these limestone samples indicate that even greater leaching of calcite could occur to give porosities in excess of 30 percent. Where dedolomitisation and pore-filling calcite are more extensive,

sub-aerial leaching has given rise to rotten dolostones seen at Griffe Grange Quarry (figure 1) and the New Harborough Farm Borehole (Ref. 243559).

(f) Traverse 8 (figure 21)

The traverse is a vertical transect, 5 metres long, across the limestone-dolostone boundary, again marked by karstification and mineralisation. The traverse was sampled at a railway cutting (Ref. 235558), adjacent to High Peak Quarry, in the Hoptonwood "Group". The crinoidal and brachiopod-rich pelsparenites and micarenites (samples 8A & 8D), which have little porosity, have become dolomitised to give a xenotopic-hypidiotopic dolostone, with a good development of calcite-filled, inter-crystalline pores. This allows the development of good dedolomitisation and leaching, which develops the higher porosities. Total dedolomitisation caused by the Late Triassic mineralisation has not increased porosity.

(g) Traverse 9 (figure 22)

The traverse is a horizontal section, 10 - 15 metres long, across the limestone-dolostone boundary in the Hopton-wood "Group" to the west of Brassington Village (figure 13) (Ref. 231543).

This is a similar example of porosity development to that in Traverse 6. Upon dolomitisation a biomicarenite with a small amount of crinoidal material has formed idiotopic-hypidiotopic dolostone with abundant intercrystalline calcite-filled pores.

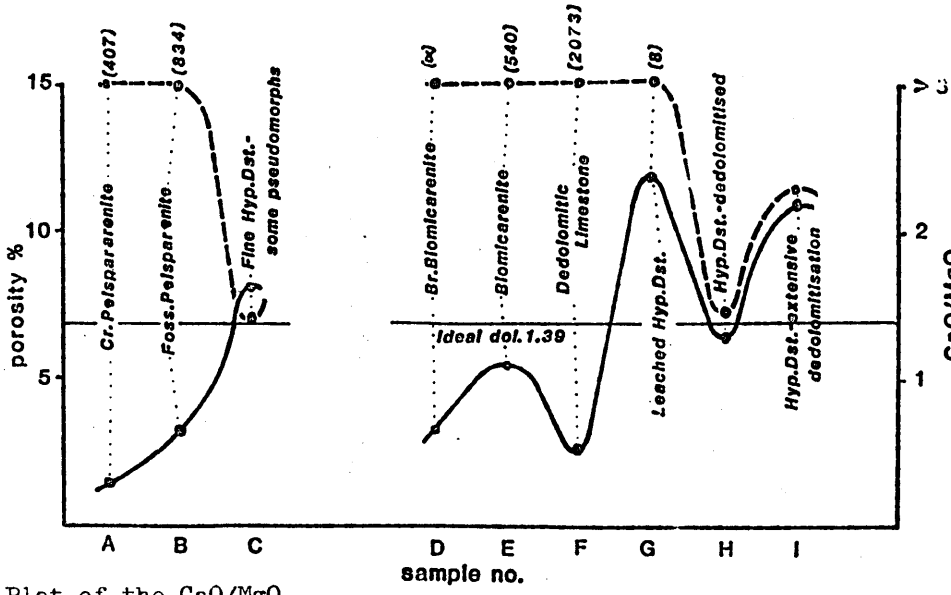


Figure 21 Plot of the CaO/MgO ratios and porosity values across the limestone-dolostone transition in a cutting adjacent to High Peak Quarry-Traverse 8

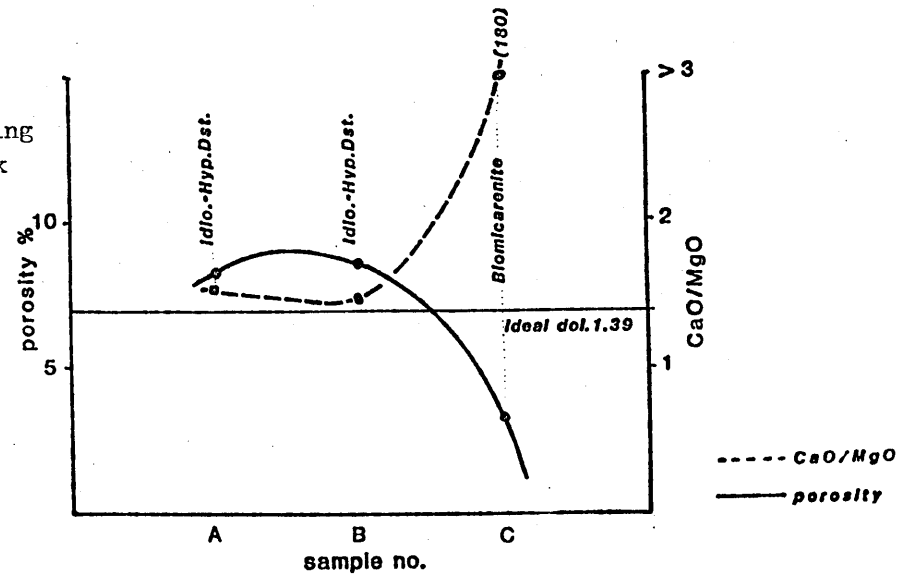


Figure 22 Plot of the CaO/MgO ratios and porosity values across the limestone-dolostone transition above Brassington village-Traverse 9

Leaching has led to a 6 percent rise in porosity, although dedolomitisation is not significant, appreciable amounts of calcite exist. It is believed that this results from poor access of meteoric waters into the formation, thus not allowing significant dedolomitisation.

(h) Traverse 10 (figure 23)

The traverse is a horizontal ground transect, 5 - 10 metres long, across the limestone-dolostone boundary, in the Hoptonwood "Group", directly north of New Harborough Farm (fig. 23) (Ref.243559).

The original crinoidal biomicarenites, samples B - F, have become dolomitised (sample A) to give typical xenotopic-hypidiotopic dolostones, which have quite high porosities due

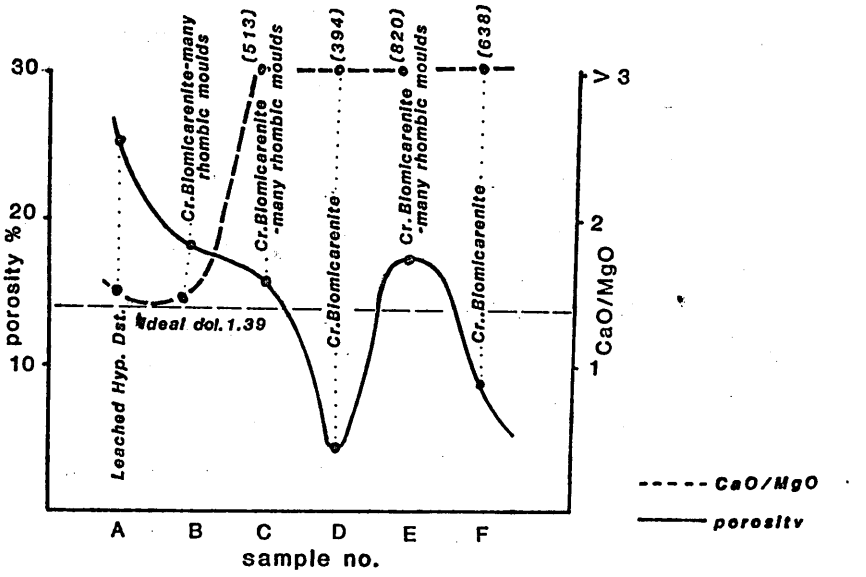


Figure 23 Plot of the CaO/MgO ratios and porosity values across the limestone-dolostone transition north of New Harborough Farm.-Traverse 10

to the leaching of pore-filling calcite and associated dedolomitisation. The low CaO/MgO ratio indicates the efficiency of this leaching. Samples 10C and 10E are "dedolomitic limestones" which are not due to mineralisation. Originally, the dedolomitic limestones represented a partially dolomitised limestone with scattered dolomite euhedra. The sub-aerial conditions and the scattered nature of the rhombs allowed their total dedolomitisation. The higher porosities of these samples are exclusively due to the leaching of the dedolomitisation calcite to give rhombic vugs. The solubility of this calcite is probably due to its higher magnesium content. This process is in direct contrast to the "dedolomitic limestone" associated

with the mineralisation , where the porosity remains low. This indicates a stabilisation of the dedolomitisation calcite to the more stable low-magnesium calcite prior to a sub-aerial exposure. Either groundwater or mineralisation may be responsible for this stabilisation of the high-magnesium calcite.

In conclusion, the foregoing data illustrate that once the dolostones have become exposed to sub-aerial weathering, the porosity development varies considerably. Higher porosities can be developed in several ways, viz. dedolomitisation, either intercrystalline, or associated with the pseudomorphs which can be an important and significant factor. The varying porosities are principally controlled by the different dolostone types outlined in Chapter IV.

(1) Xenotopic Dolostone

These dolostones are totally dolomitised limestones consisting of interlocking mosaics of dolomite, giving low porosities. The only porosity present in these samples is probably inherited from the original limestone. (Traverses 1 and 2). However, if crinoidal pseudomorphs occur then under sub-aerial conditions these can become dedolomitised and leached to give a good vuggy porosity (Traverses 4 and 5). This is indicated by the "cheesy" texture shown by most weathered outcrops.

(2) Xenotopic-Hypidiotopic and Idiotopic Dolostones

Both dolostone types represent incomplete dolomitisation of sparry calcite, giving mouldic and intercrystalline pores (Section 4.4.1). At the periphery of the dolostone outcrop incomplete dolomitisation (see Traverse 1 and 3) may be the result of a dwindling magnesium supply during the latter stages of the dolomitisation process. Dolostones showing extensive pore-filling calcite shows very variable porosities. Where "aggressive" meteoric solutions have not had ready access, i.e. away from solution-affected bedding and jointing, although significant amounts of calcite occur, leaching is poor and thus low porosity exists, as is seen in Traverses 1, 2 and 3. In a more suitable environment, such as that occurring just below the soil horizon, due to slightly acidic rainwater or slightly more aggressive water seeping from the thin soil cover (Section 4.4.5), leaching and dedolomitisation may occur to a greater extent. Similar areas of excessive dedolomitisation and leaching may be shown to occur next to karst channels, such as bedding, jointing, unconformities and stylolites, where again aggressive waters have access to local units.

Dedolomitisation has played a significant role in the development of porosity. Certainly, dedolomitisation of crinoidal pseudomorphs produce spectacular porosities, even without the aid of intercrystalline pores as seen at Harborough Rocks (pl. 31a). Peripheral intercrystalline dedolomitisation is more localised than crinoidal dedolomitisation, due to the apparent ease with which the crinoidal fragments are altered (Section 4.4.5). Intercrystalline

dedolomitisation occurs in many samples, but only becomes significant where there is sufficient pore-filling calcite and easy access of aggressive waters such as in incompletely dolomitised dolostone occurring at the surface or close to a channelway at depth. In these cases, leaching of the dedolomitisation calcite may supply a significant amount to the porosity. Extensive dedolomitisation and leaching lead to a very rotten dolomite, which is easily abraded and removed by streams, causing a widening of karst channels. More completely dolomitised samples have less free calcite and consequently dedolomitisation is less significant and leaching will cause a regeneration of the primary dolostone porosity (Section 5.2).

(3) Dolomitic Limestones

The partially dolomitised limestones (Section 4.4.1(4)) possess a characteristic type of porosity which is the product of the scattered nature of the rhombs. This allows extensive dedolomitisation which upon leaching gives rhombic vugs (sample 10C). The greater solubility may indicate the presence of high-magnesium calcite formed during dedolomitisation, suggesting a recent origin. An earlier origin may have allowed the high-magnesium calcite to become stabilised to low-magnesium calcite, rendering it less soluble. The other example of dedolomitic limestone is associated with mineralisation, and this shows no development of rhombic vugs or any suggestion of a greater solubility. This is due to stabilisation to a low-magnesium calcite either during or after mineralisation.

These ten traverses illustrate the manner in which

samples are leached at or very close to the present-day surface, where there is an abundant supply of aggressive water. At depth within the dolostone succession, the access of aggressive water is more localised, possibly along solution-widened bedding, joints, stylolites, etc.. A number of boreholes were studied in the context (fig. 13).

The borehole material was studied using thin sections, whole rock Energy Dispersive X-r-f analysis (Appendix VI) and porosity determinations using core and chip samples (Appendix IV). The Harborough Rocks Boreholes consist only of porosity and calcite profiles, unfortunately no samples were available for a detailed petrographic study, thus the information gained from these boreholes is limited.

5.3.2. New Harborough Farm Borehole (Ref. 243559)

The borehole was drilled in November 1979 by the writer in conjunction with an Aston University drilling team, using a Minute Man drilling rig (pl. 29a). It was drilled to a total depth of 15 metres and penetrated well-bedded dolostones of the Hoptonwood "Group" (figure 24). The succession of dolostones essentially consists of xenotopic-hypidiotopic dolostones with rare idiotopic dolostones. Towards the bottom of the hole dedolomitic limestone, caused by mineralisation, occurs. The majority of the dolostones have porosities between 5 and 10 percent (see figure 24). These are above the expected values, as one would expect lower values due to the occlusion of primary dolostone porosity by pore-filling

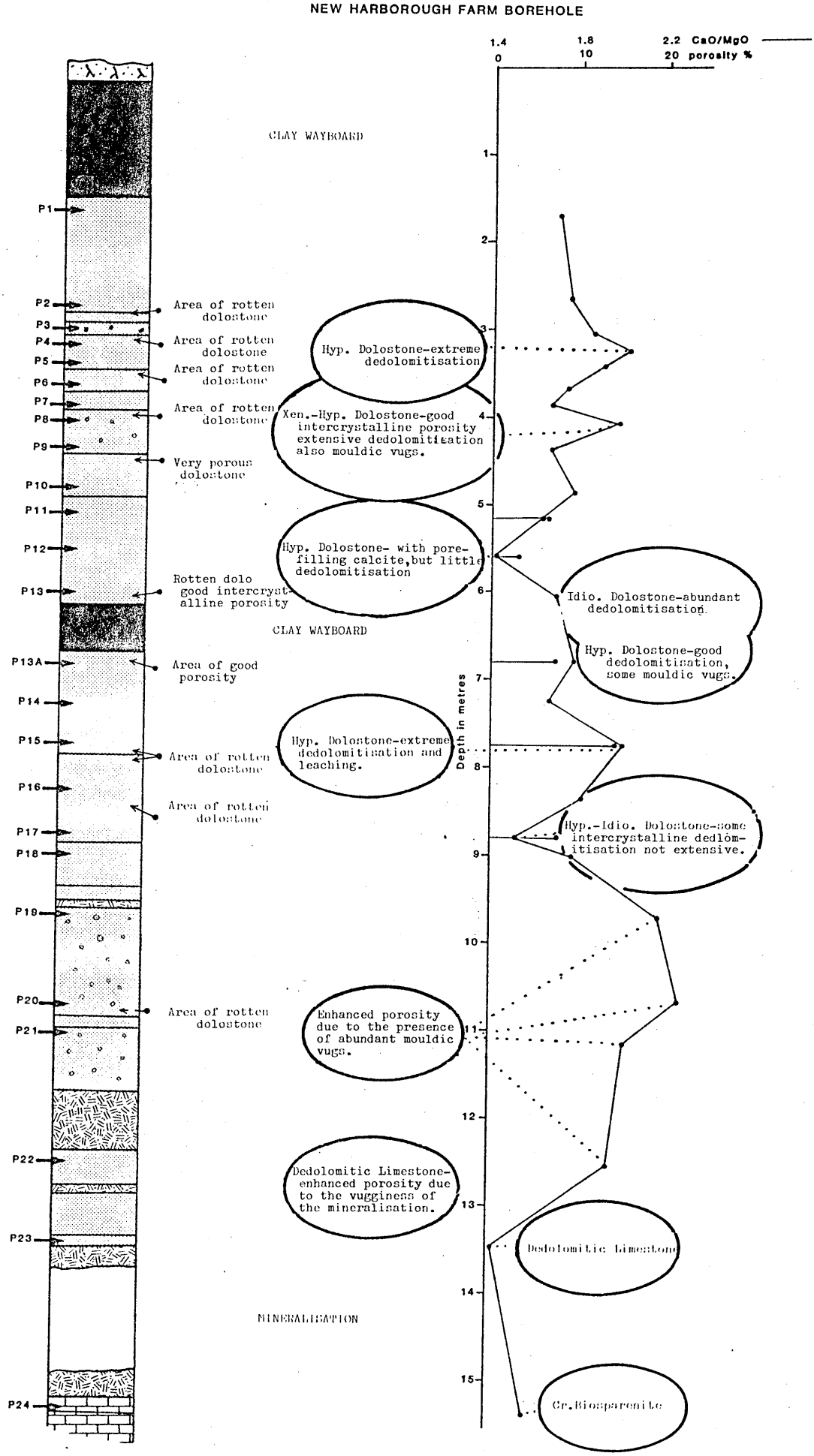
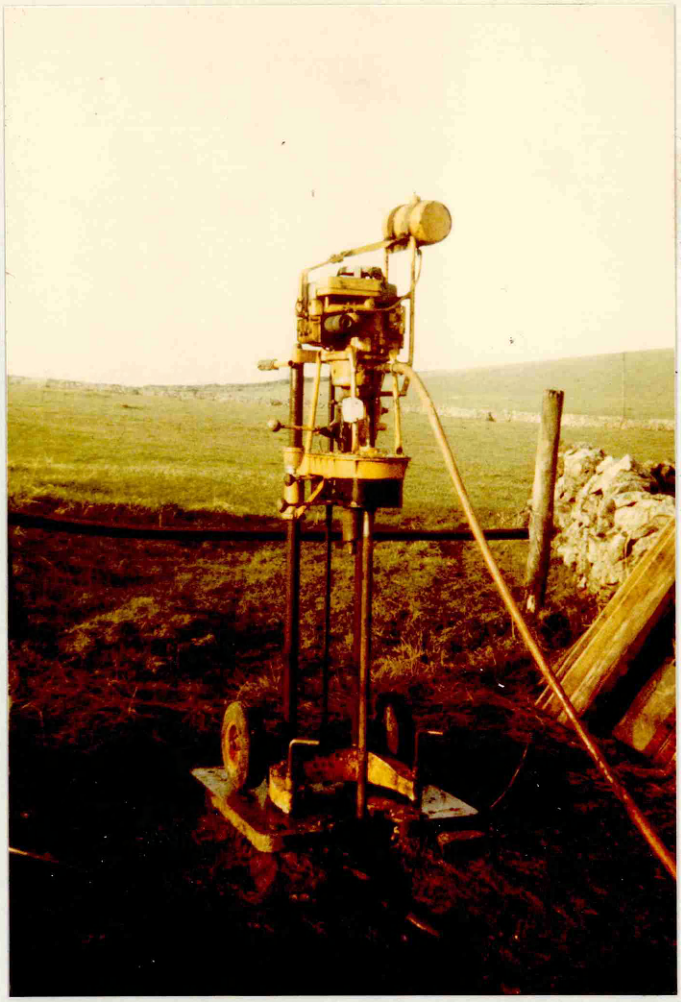
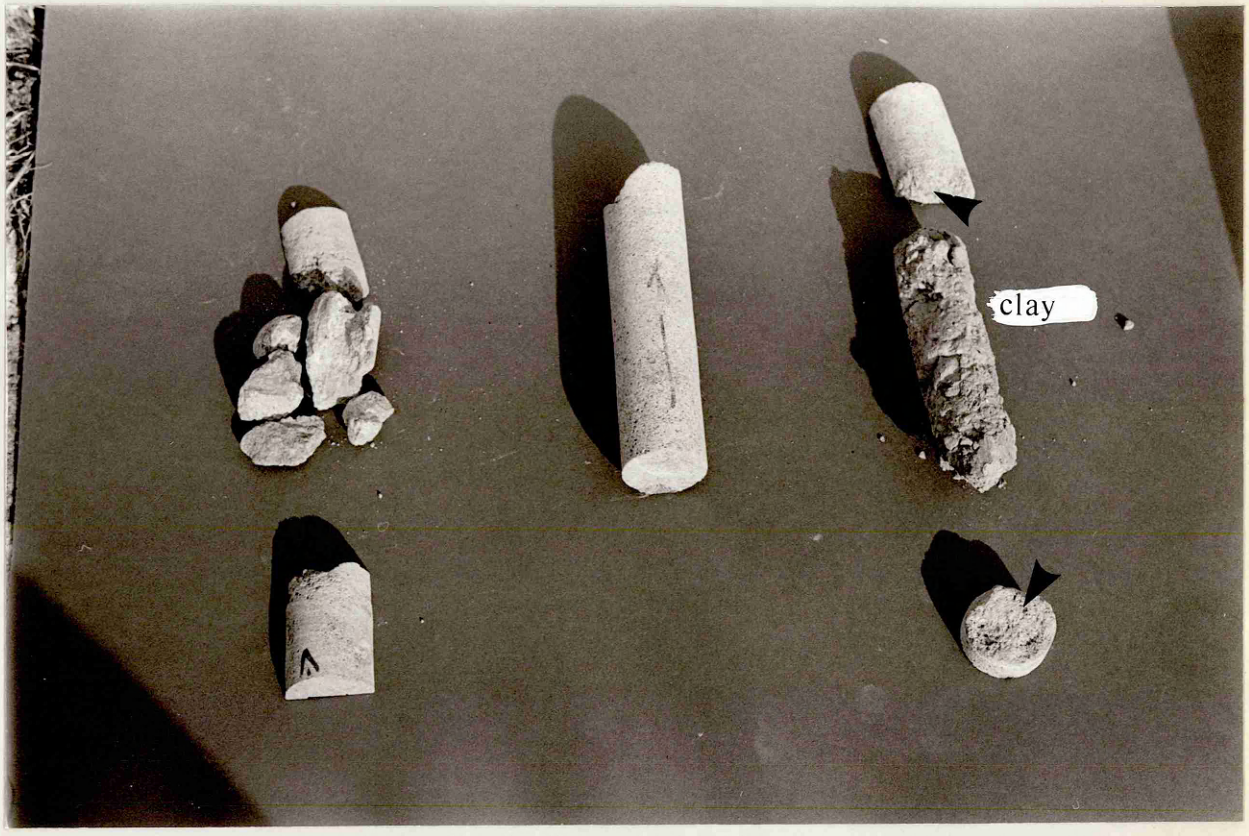


Figure 24 Logs of CaO/MgO ratio, porosity and lithology in the New Harborough Farm Borehole



a



b

Plate 29 (a) Minute-Man drill in working position, over the New Harborough Farm Borehole and (b) part of the core from the New Harborough Farm Borehole showing a rotten zone (broken core) and clay associated with upper and lower porous dolostone. -1" diameter core.

calcite. This suggests that dissolution has occurred to a certain extent throughout the formation.

Figure 24 shows that a number of very localised areas of rotten dolostone (pl. 29b) which consist of a very soft, in some cases sandy-looking, material and must represent extreme leaching of the dolostone. These intervals appear to be horizontal and parallel to bedding. The analysis of this material was impossible due to its very friable nature and thus more coherent samples adjacent to these areas were taken. These samples show good dedolomitisation and an increase in porosity (figure 24), although in samples P4, 8, 13, 15, 16 and 20 these are very extensive. Inter-crystalline dedolomitisation occurs (Section 4.4.5) to some extent in most dolostones in the borehole which have excess calcite but is restricted to the edges of the pores. The extensively dedolomitised samples show peripheral dedolo-mitisation (i.e. around calcite-filled pores), as well as extensive matrix dedolomitisation (figure 10) (Section 4.4.5). This may be due to the good supply of aggressive water (also causing leaching) along zones of rotten rock. These samples have up to 15 percent porosity, showing the presence of effective solution associated with these zones. As indicated by the CaO/MgO ratio and high porosity of sample 15 (figure 24), further leaching could lead to the development of a very rotten dolostone.

The lack of low values of porosity in the dolostones of this borehole is explained by the lack of xenotopic

dolostone within the Hoptonwood Group and also by the effectiveness of leaching throughout the borehole. Samples P12 and P17 do show a much lesser degree of leaching which is due to the lack of crinoidal pseudomorphs,. The much higher porosities in the Hoptonwood succession may be, in part, caused by the greater solubility of dedolomitised crinoidal pseudomorphs, which must have provided greater access to the remainder of the rock. Beds lacking crinoidal pseudomorphs are incompletely dolomitised, and have lower porosity.

The CaO/MgO ratios show that many samples have a high free calcite content, indicating their potential for dedolomitisation and leaching. Much of the porosity is simply a regeneration of the primary dolostone porosity, although where dedolomitisation is extensive then more irregular vugs occur. Even upon removal of the total calcite, dissolution of the dolostone continues because of its slight solubility. It may also proceed if saturated solutions are available to cause dedolomitisation (Section 4.4.5) without the aid of indigenous calcite.

It has been mentioned that crinoidal pseudomorphs contribute greatly to the higher porosity values of the core due to their enhanced solubility, once they have become dedolomitised. This is the reason for the higher porosities in the lower part of the borehole (figure 24), due to the abundance of the pseudomorphs.

The lowest part of the borehole is marked by a mineralised cavity formed along the limestone-dolostone boundary (see Section 6.1.). The dolostone above the cave has become totally dedolomitised (figure 24) to give a coarse sparry calcitic rock. As in Traverse 6 (Section 5.3.1(d)) the dedolomitic limestone shows little porosity, in contrast to the dedolomitic limestones associated with partially dolomitised limestone (Section 4.4.1(4)).

The clay wayboard at 6.2 - 6.7 metres has been responsible for the localisation of dedolomitisation and leaching, above and below the clay. The clay surface acted as an impermeable barrier, causing solutions to flow along the junction, giving a perched water table. The aggressive nature of these waters would allow the necessary dedolomitisation and leaching to occur above the wayboard. This does not extend far into the overlying dolostone due to its idiotopic nature, with sufficient calcite present to inhibit effective leaching (Section 5.2.). Below the wayboard another area of rotten dolostone occurs, although saturation would be less likely. The higher calcium content is thought to be due to incomplete dolomitisation caused by the protective nature of the clay during dolomitisation. The solution of the pore-filling calcite to give the rotten dolostone, is caused by solutions seeping through the clay which become charged with sulphuric acid, developed from the oxidation of pyrites.

The study of this borehole allows the identification of the features described in the traverses, and these can be

studied at depth within the dolostone succession. Karstification has been shown to have an important role; solution-affected bedding, small joints and fractures give aggressive water greater access to the succession since they allow localised porosity enhancement along the karst channels. The extent of dedolomitisation and leaching depends heavily upon the dolostone fabric. A xenotopic dolostone, with little or no calcite, remains quite resistant, even when forming a wall of a karst channel. The more xenotopic-hypidiotopic and idiotopic dolostone have various amounts of pore-filling calcite. Where calcite is common, dedolomitisation and leaching are abundant and give rise to a very rotten dolostone. Less calcitic samples of dolostone give rise to quite a porous dolostone, but still retain their coherence.

5.3.3. Monyash Borehole S.E. 4 (Ref. 170625)

A detailed study of the Matlock Group is difficult in the study area, due to the lack of good sections. Thus, equivalent Brigantian limestones (i.e. the Monsall Dale Limestone) cropping out to the north of the study area at Monyash, were studied by sampling borehole material supplied by the I.G.S.. The dolomitisation appears to be epigenetic, clearly transgressing the Albian/Brigantian stratigraphic boundary, similar to that seen in the Wirksworth area. The lithologies of these limestones are similar to the Matlock Group, consisting essentially of brachiopod-rich biomicarenites and sparenites.

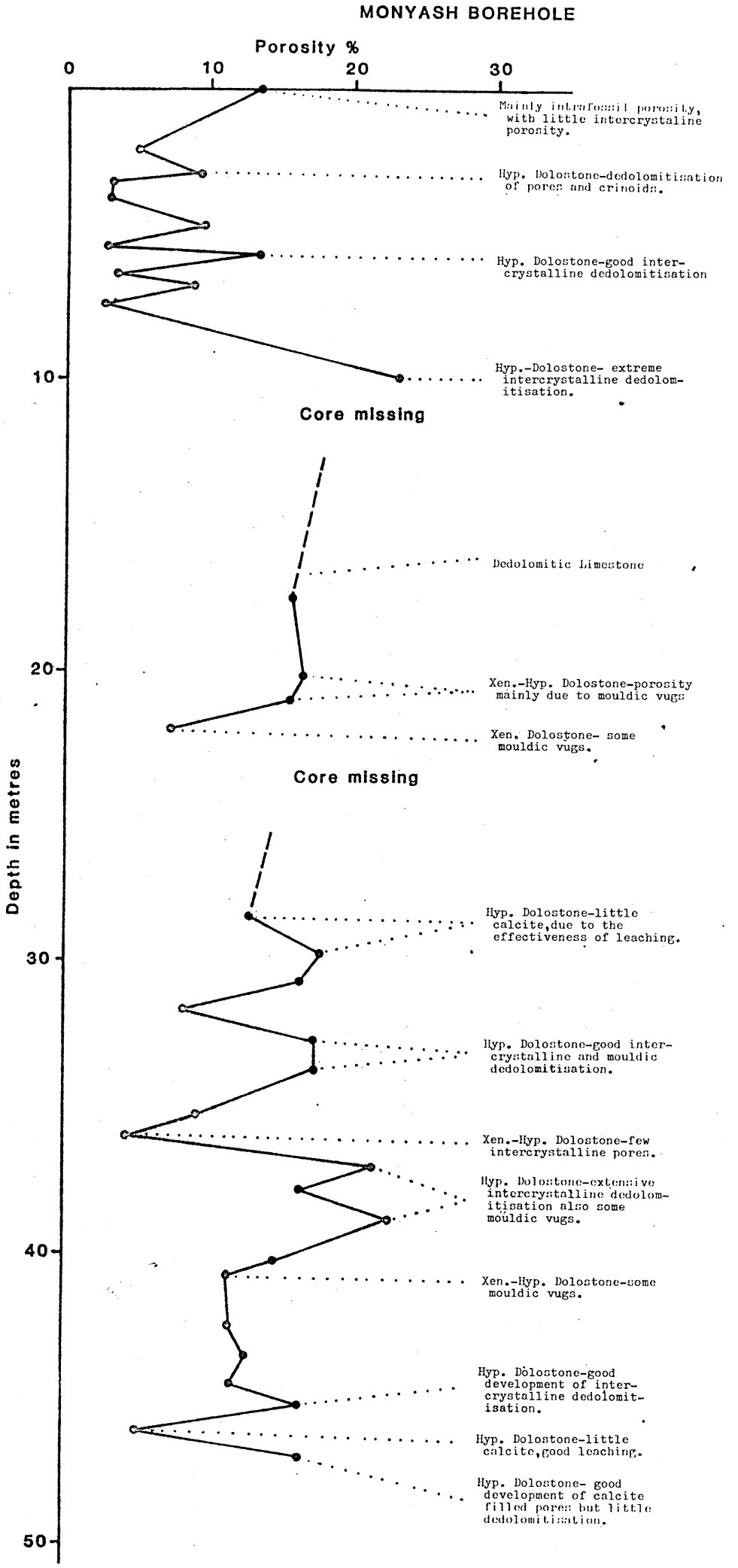
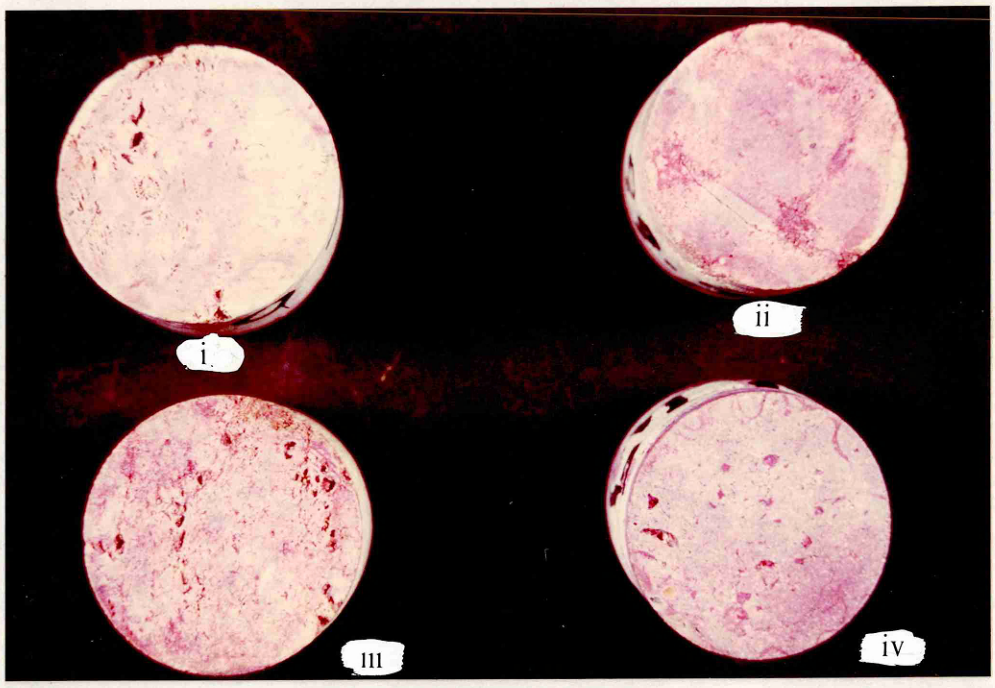
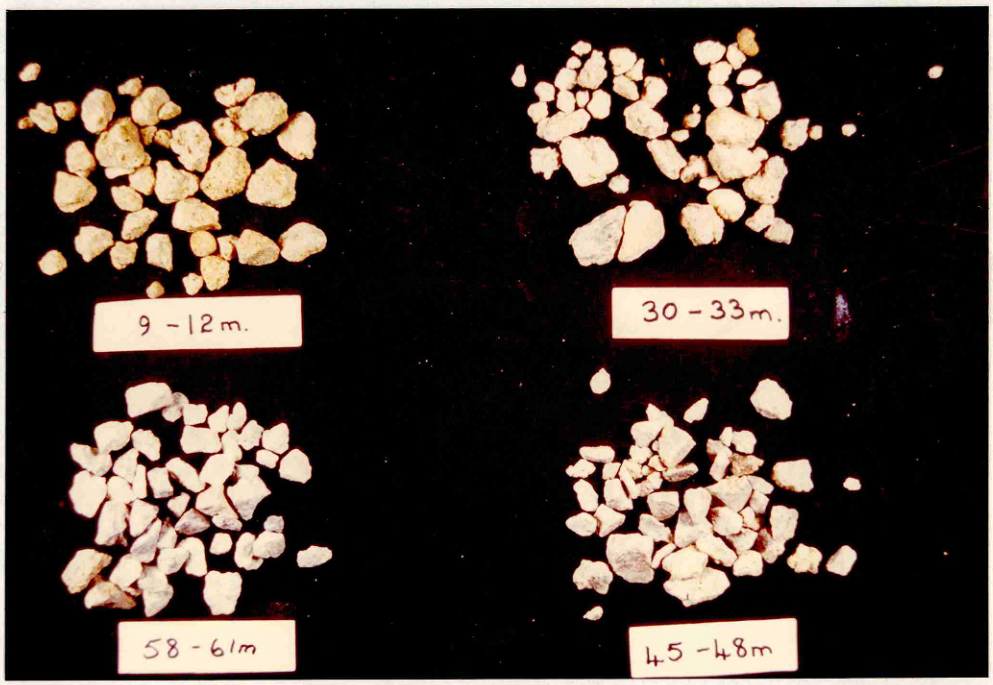


Figure 25 Porosity log of the Monyash Borehole,which includes brief summaries of the different areas of porosity development.

Plate 30 Borehole samples (a) cores from the Monyash Borehole(1" diam.) which have been stained to indicate the presence of dedolomitisation and calcite-filled pores i- mouldic porosity 0-2.15m. ii- intercrystalline dedolomitisation 7-8m iii-intercrystalline and mouldic porosity 32m. iv - intercrystalline and mouldic dedolomitisation and leaching 40m. and (b) drill chips from the Ryder Point Borehole indicating the rusty colour and greater porosity(9-12m) due to dedolomitisation.



a



b

The upper part of the core is composed of xenotopic-hypidiotopic dolostone with varying amounts of pore-filling calcite (figure 25). The variable porosity is caused by the presence of dedolomitised pseudomorphs, intrafossil porosities and possibly good enhanced porosities associated with dedolomitisation (36 - 40 metres).

The middle and lower parts of the borehole give consistently more porous samples. The higher general porosity is probably due to the dedolomitisation of crinoidal pseudomorphs (as in the New Harborough Farm Borehole), which occur to a certain extent throughout the borehole. Areas of good porosity can be related to localised leaching, probably having a similar origin to the rotten areas of the New Harborough Farm Borehole, i.e. next to karst channels, where a good access of fluids occurs (Section 5.3.1(2)). These dolostones either show little calcite, but have good porosity (eg. 29.5 - 31.0 metres) indicating the effectiveness of leaching; or show excessive dedolomitisation and associated leaching (32.5 - 34.0 metres and 37.0 - 39.0 metres). The areas of lower porosity, although containing reasonable amounts of calcite, represent areas where there is little access of fluids (Traverses 1 and 2), and thus only minor dedolomitisation and leaching has developed. In more favourable situations adjacent to karst channels, the latter dolostones would promote ample dedolomitisation and leaching.

The core loss seen in the profile (figure 25) probably indicates the occurrence of caves, associated with mineralisation,

which is suggested by the dedolomitic limestone occurring below both gaps. Other karst features, such as solution-widened bedding, may be the reason for the enhancement of porosity in the lower part of the borehole (figure 25).

5.3.4. Harborough Rocks Section (Ref. 243553)

A sequence of samples was taken down the face of Harborough Rocks to study the petrography and porosity development of the dolostone in this very exposed setting. The results are shown in figure 26 . The porosity of the dolostones is dominated throughout by mouldic vugs, resulting from the leaching of dedolomitised crinoidal pseudomorphs (Section 4.4.5) some showing remnant optically-continuous rims (pl.31a). Few examples of the dedolomitisation calcite remain, however where these occur they show typical anhedral dolomite remnants, enclosed within large poikilotopic calcite crystals. The very high porosities are produced by extreme alteration of these pseudomorphs. Intercrystalline pores contribute little to the total porosity of the dolostones, due to the former xenotopic nature of the crinoidal-rich dolostone. Where intercrystalline pores exist, these are totally leached due to the excess porosity and permeability introduced by the mouldic vugs. H.R.10 represents a sample where modified intercrystalline pores contribute mainly to the porosity. The very enhanced porosities of the whole sequence are due to the very exposed nature of the face. A corresponding enhancement can be seen within boreholes penetrating Harborough Rocks (Section 5.3.6.), which implies a recent origin for the dedolomitisation of the pseudomorphs.

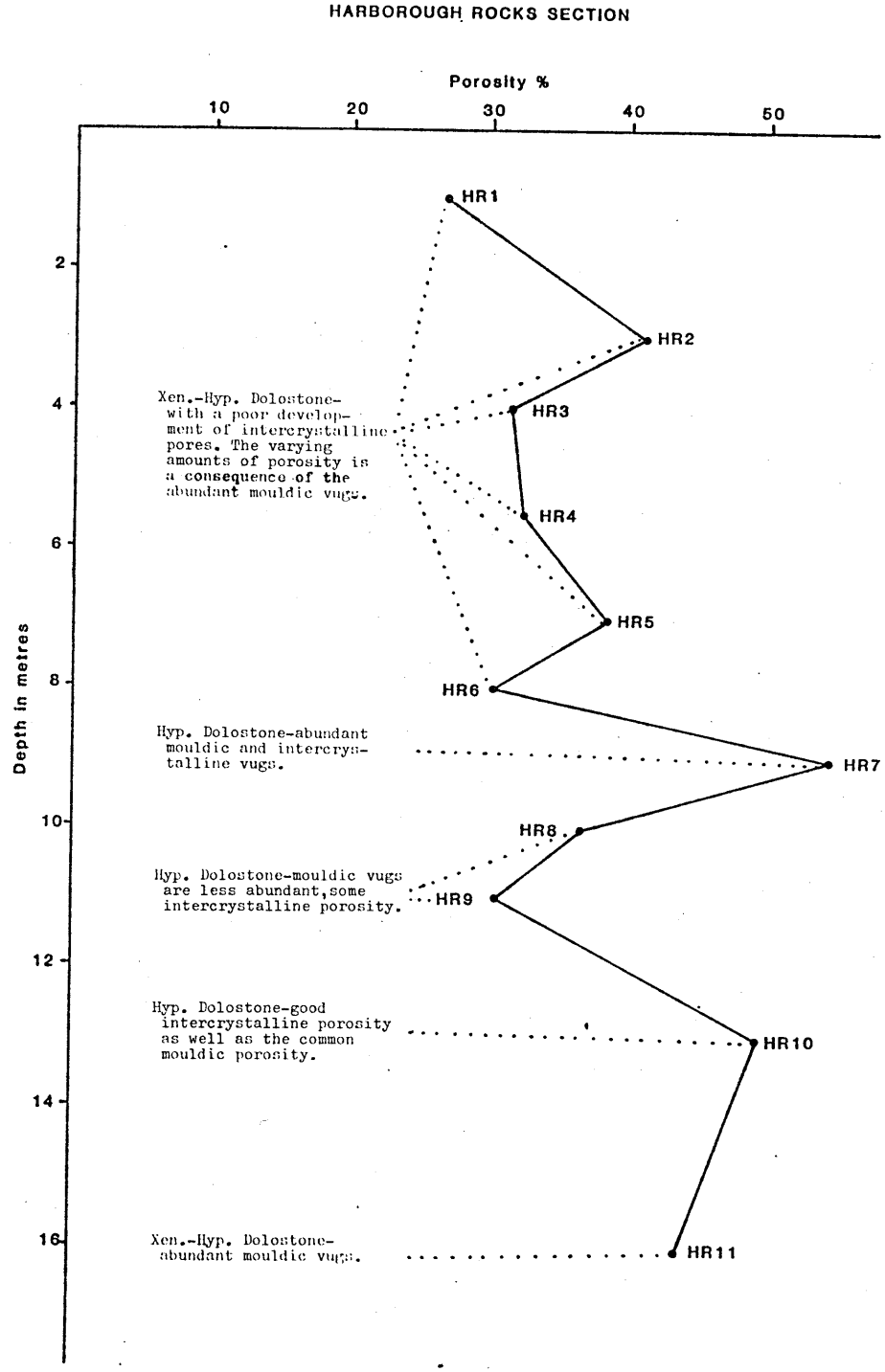


Figure 26 Porosity log of the Harborough Rocks Section including brief summaries of the porosity development.

5.3.5. Ryder Point Borehole (Ref. 060547)

The borehole was drilled in 1978 by Dresser Minerals in the grounds of the Ryder Point Plant and penetrated dolostones of the Hoptonwood Group. The samples consisted of quite coarse drill cuttings (giving their own unique problems during analysis, see Appendix IV) taken at three metre intervals. This sample spacing allows little indication of the very localised porosity development such as that noted in the New Harborough Farm Borehole. Nonetheless, variation in the porosity and CaO/MgO profiles can be related to the features noted in the traverses and other boreholes.

The upper 40 metres shows higher overall porosity (20 - 25 percent), yet it retains a similar variation to the remainder of the borehole (figure 27). The higher porosity may suggest that the generally enhanced porosities seen in the other boreholes near the surface (Section 5.3.6) may decrease with depth. The increase in porosity values (109-112 metres) reflects areas of greater leaching associated with bedding and jointing. The great majority of the dolostones are xenotopic-hypidiotopic, containing varying amounts of calcite-filled pores, crinoidal pseudomorphs and dedolomitisation. Dedolomitisation and leaching occur to a certain extent, but both features give locally high values (see figure 27), as noted elsewhere associated with bedding planes.

At a depth of 3 - 6 metres (figure 27) there is a zone of extensive dedolomitisation, due to aggressive surface waters (Section 4.4.5), although, strangely, relatively little

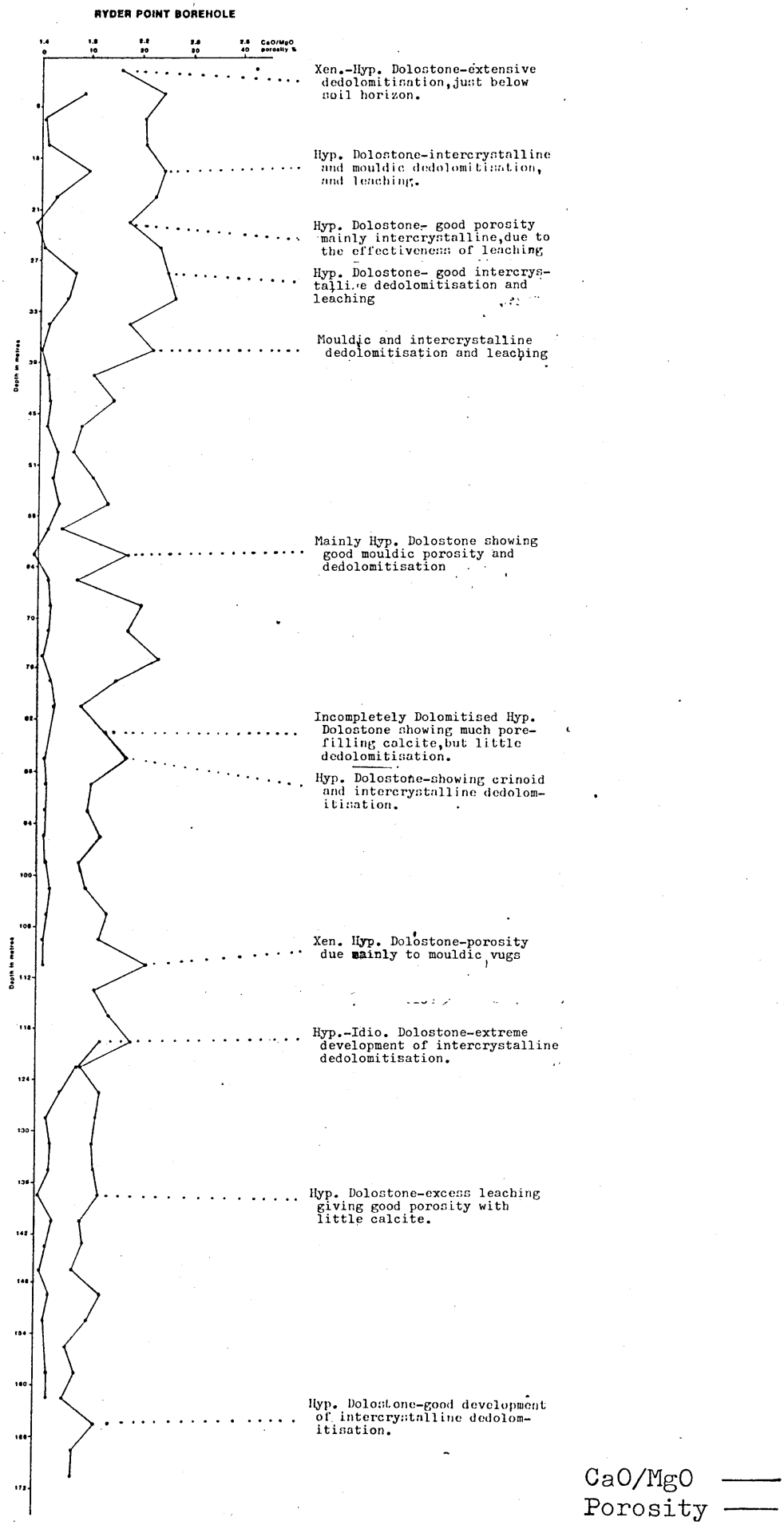
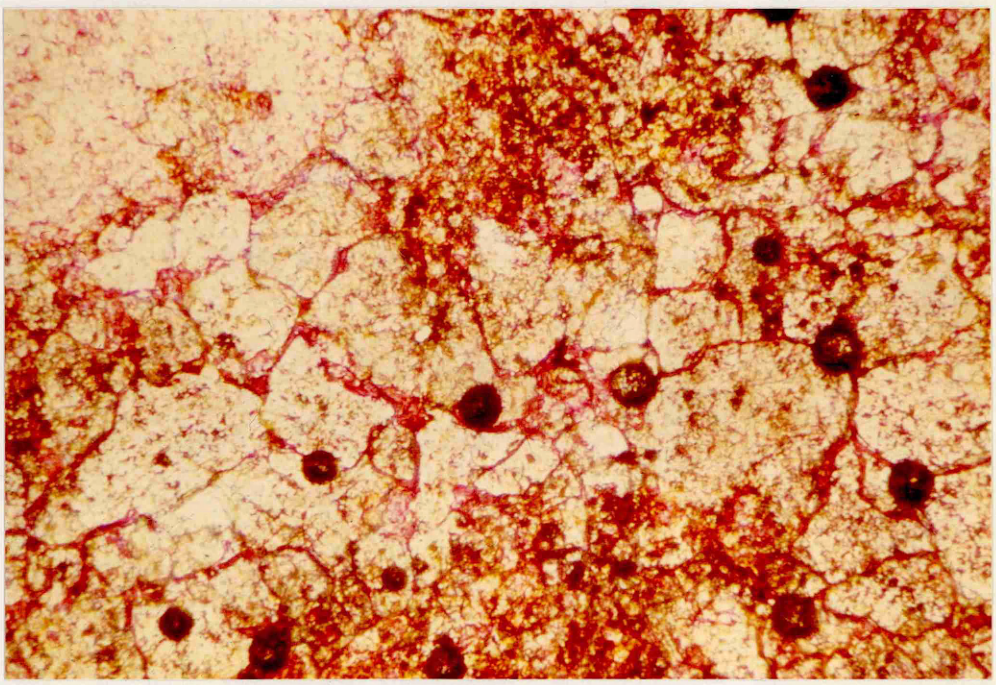


Figure 27 Porosity and CaO/MgO logs of the Ryder Point Borehole, including brief summaries of the porosity development.

a



b

Plate 31 (a) Mouldic porosity at Harborough Rocks, H."Group", showing a remnant synbaxial rim(fragments 1-2cms.) and (b)intercrystalline dedolomitisation, marked by the pink staining. sample 3-6m Ryder Point Bh. H.Gr. x80

porosity has developed. Formerly the sample consisted of a xenotopic-hypidiotopic dolostone with a good amount of calcite-filled pores, which in the presence of aggressive meteoric water allows extensive dedolomitisation, even within the interlocking matrix (plate 31b).

At depths of 12 - 15 metres, 24 - 30 metres, 118 - 121 metres and 163 - 166 metres (figure 27) corresponding rises in the porosity and CaO/MgO profiles occur. The petrography indicates that the greater CaO/MgO is due to the dolostone type, i.e. idiotopic (Section 4.4.1(3)) and an increase in dedolomitisation (intercrystalline and pseudomorphs); an especially good example occurs between 118 - 121 metres. As indicated in Chapter IV both the dedolomitisation and leaching are related to a similar supply of aggressive waters along bedding planes and jointing (figure 10).

The intervals between 61 - 64 metres and 136 - 139 metres (figure 27) show a high porosity with the corresponding fall in the CaO/MgO ratio, suggesting that areas of excessive leaching exist where the original pore-filling and dedolomitisation calcites have been removed. Other marked changes can be found at 21 - 24 metres, where there is a slight decrease in the porosity profile. The sample shows little calcite, due to its removal by leaching, thus allowing only a limited increase in porosity to occur. The rise in the CaO/MgO ratio at 82 - 85 metres is principally caused by the presence of a less completely dolomitised xenotopic-hypidiotopic dolostone and associated dedolomitisation. The rise between 61 and 88 metres is

caused by the greater abundance of crinoidal material, mainly from the dedolomitisation of the crinoidal pseudomorphs.

5.3.6. Harborough Rocks Boreholes (figures 28 - 36)

Figures 28 - 36 represent porosity and calcite profiles of seventeen boreholes drilled within the Harborough Rocks area by Steetley Minerals Ltd. in the 1950's. Unfortunately, no core material was available for a detailed petrographic study. However, from the foregoing details of the other boreholes, some idea may be obtained from the calcite and porosity profiles. The free calcite percentage has been calculated assuming the dolomite to be stoichiometric (Table VI) The boreholes penetrate the massively-bedded dolostones of the Hoptonwood Group, with abundant crinoidal dolomite pseudomorphs.

The great majority of the porosity profiles remain reasonably constant with depth, indicating a good degree of dissolution throughout the drilled interval. In contrast, the calcite profiles vary considerably, rising and falling quite sharply with no corresponding deflection in the porosity profile. The calcite profiles reflect the completeness of the dolomitisation (Sect. 4.4.1.), giving varying types of xenotopic-hypidiotopic and idiotopic dolostones, and the extent of dedolomitisation. The much higher calcite values may represent the idiotopic dolostones, extreme dedolomitisation or mineralisation. The full details of each borehole can be found in the summaries of figures 28 - 36 . Many features noted in the previous boreholes and sections can be found. However, the great detail of the New Harborough Farm Borehole

HARBOROUGH ROCKS

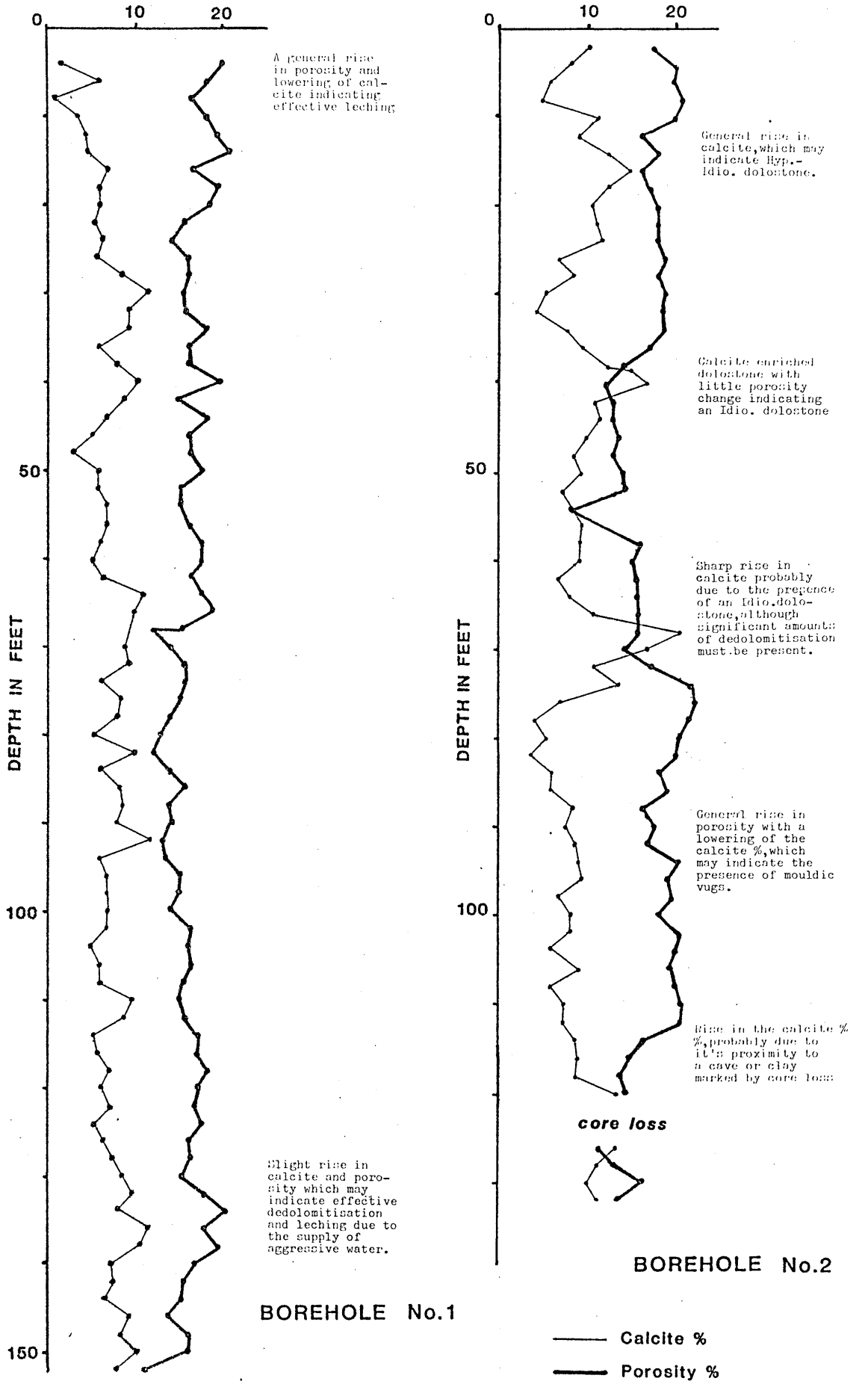


Figure 28 Porosity and calcite logs plus brief summaries of Harborough Rocks Boreholes Nos.1 & 2

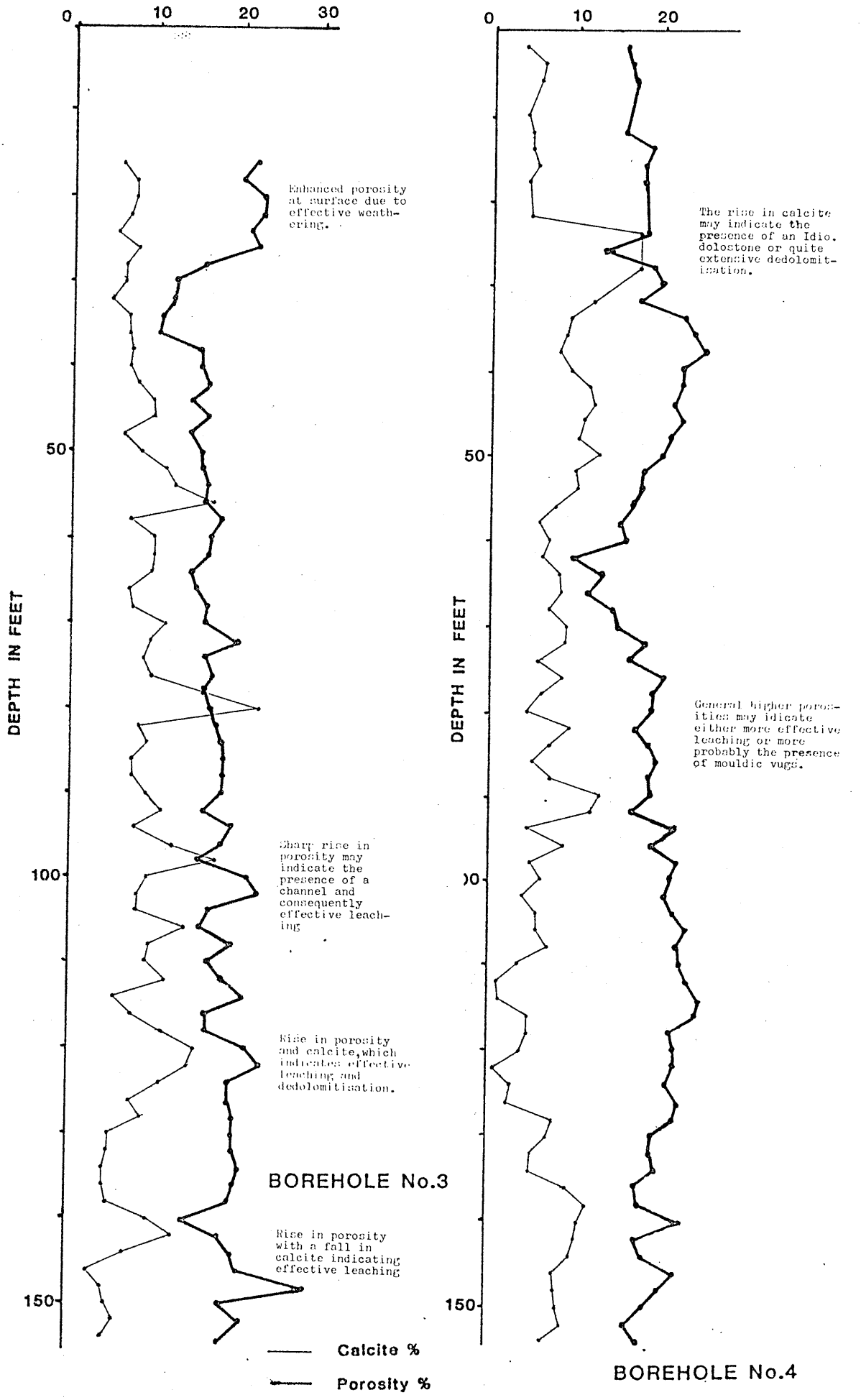


Figure 29 Porosity and calcite logs, plus brief summaries of Harborough Rocks Boreholes Nos. 3 & 4

HARBOROUGH ROCKS

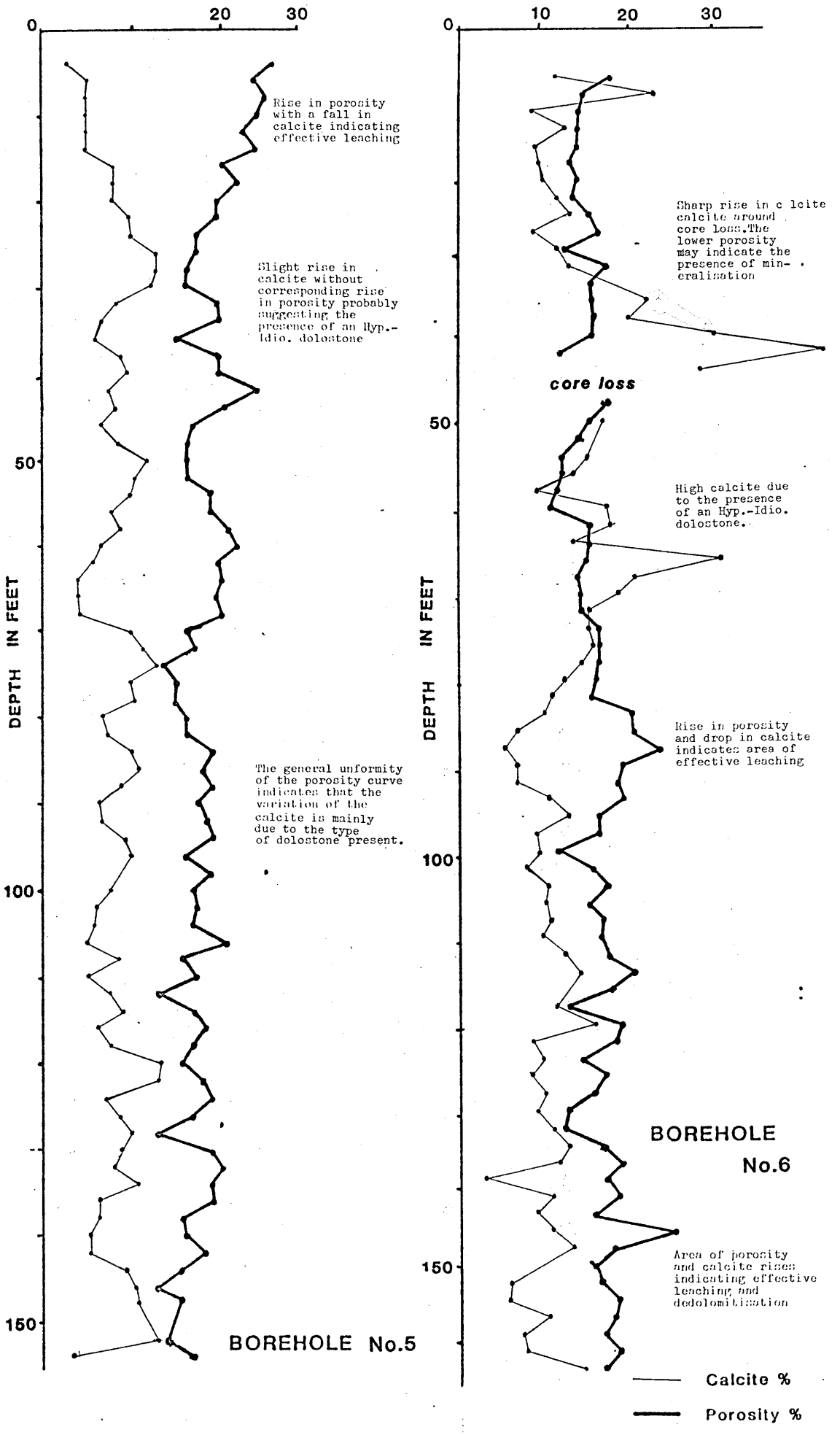


Figure 30 Porosity and calcite logs ,plus brief summaries of Harborough Rocks Boreholes Nos. 5 & 6

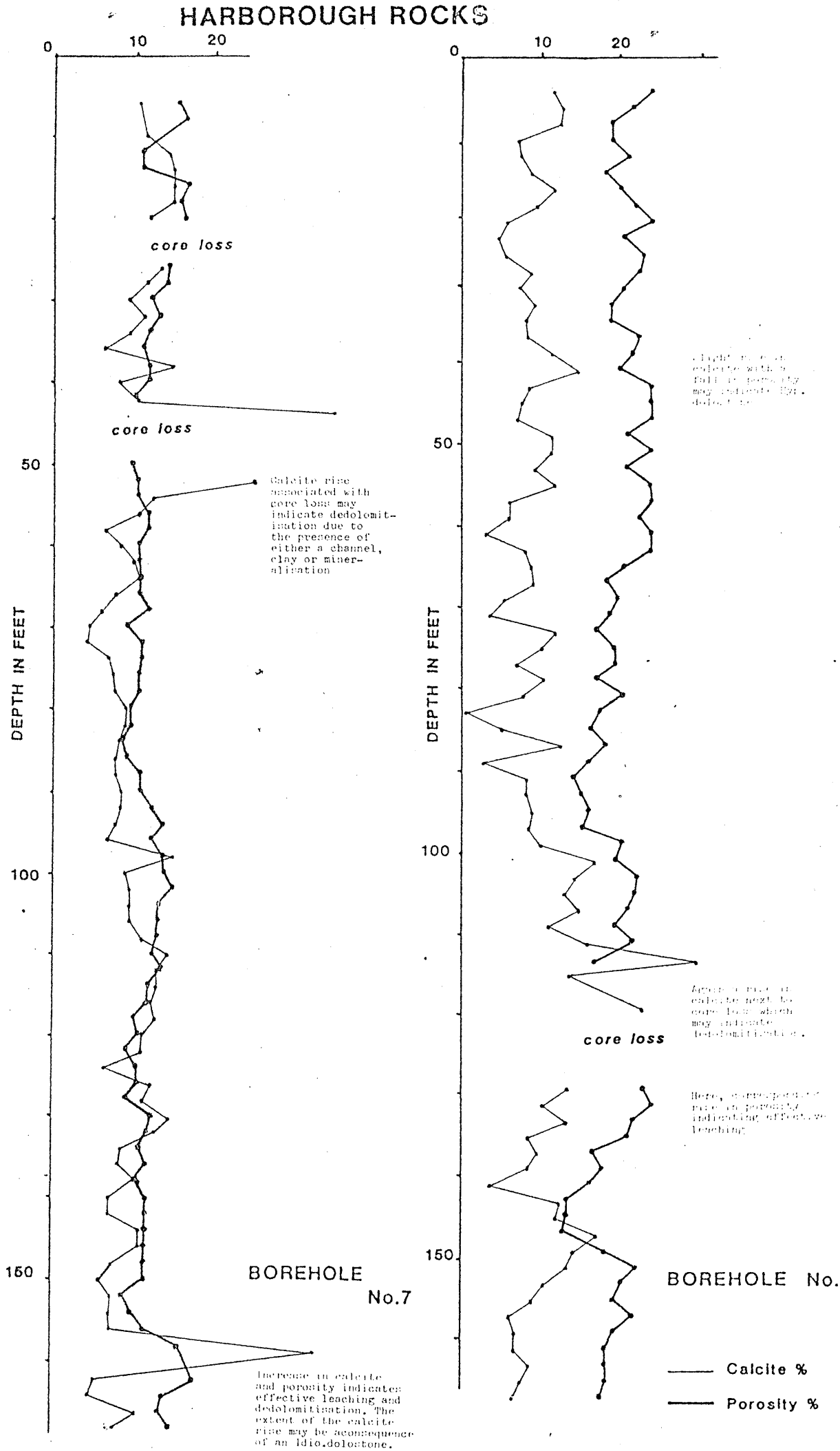


Figure 31 Porosity and calcite logs, plus brief summaries of Harborough Rocks Boreholes Nos. 7 & 8

HARBOROUGH ROCKS

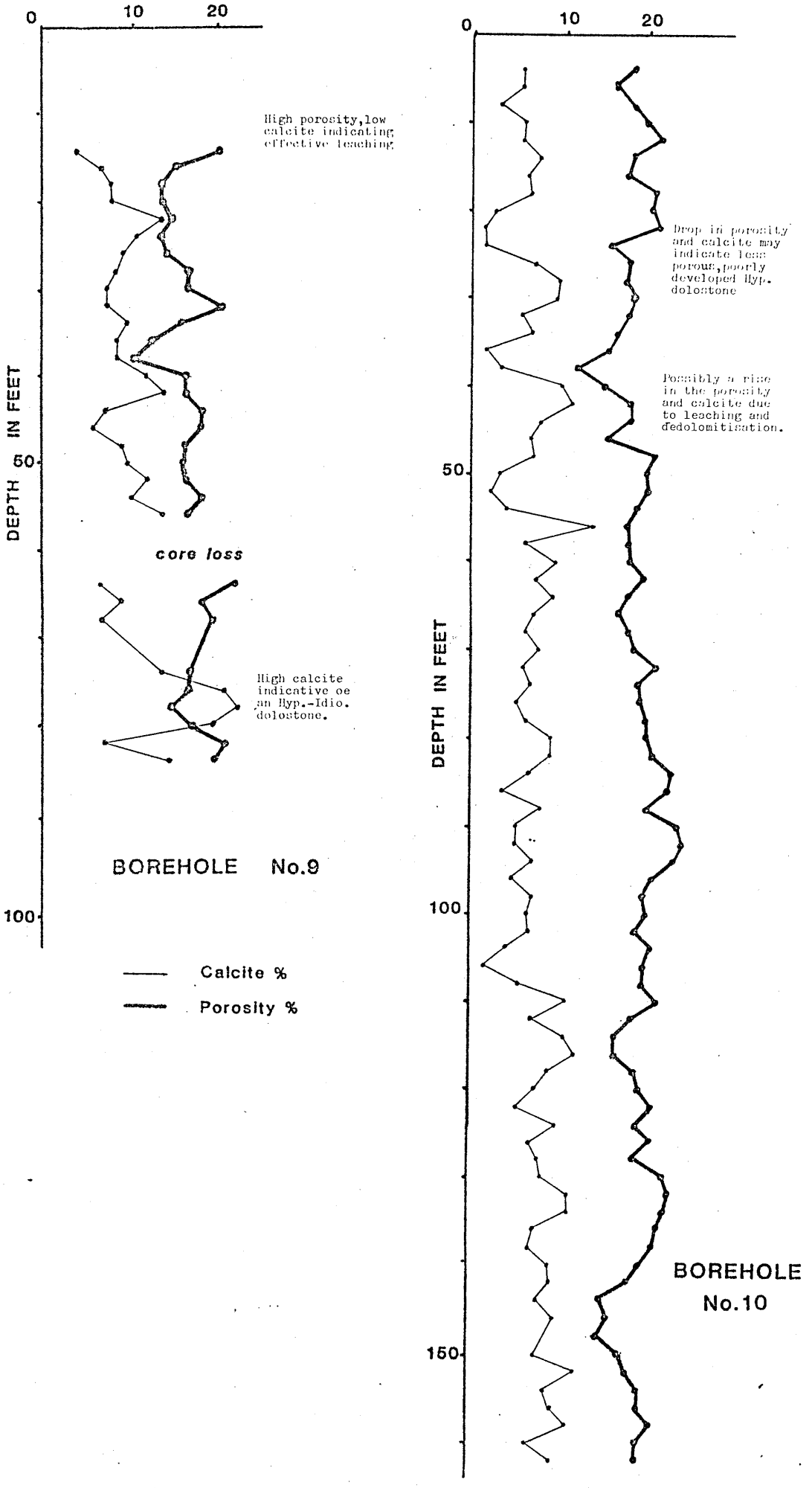


Figure 32 Porosity and calcite logs, plus brief summaries of Harborough Rocks Boreholes Nos. 9 & 10

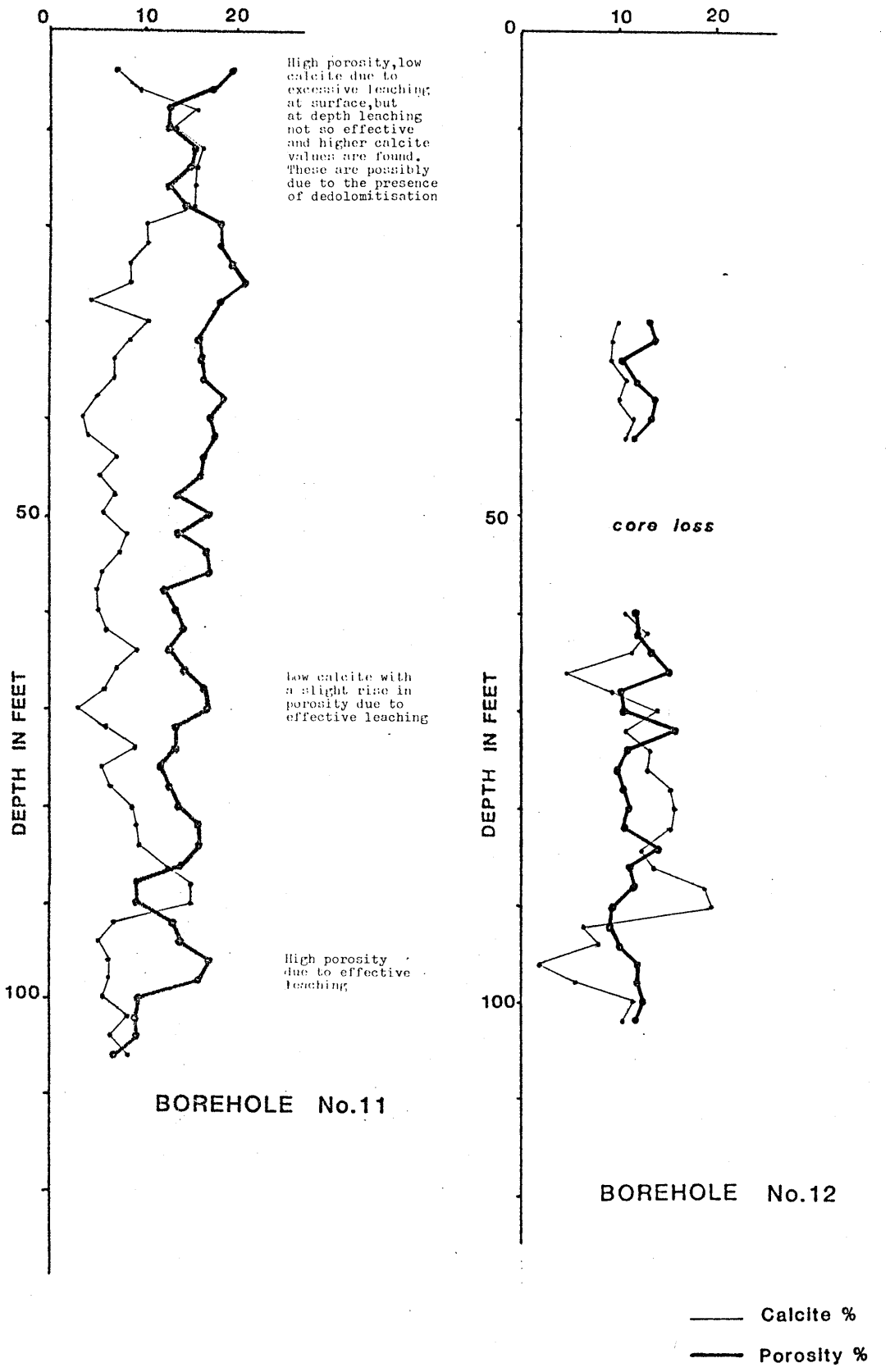


Figure 33 Porosity and calcite logs, plus brief summaries of Harborough Rocks Boreholes Nos. 11 & 12

HARBOROUGH ROCKS

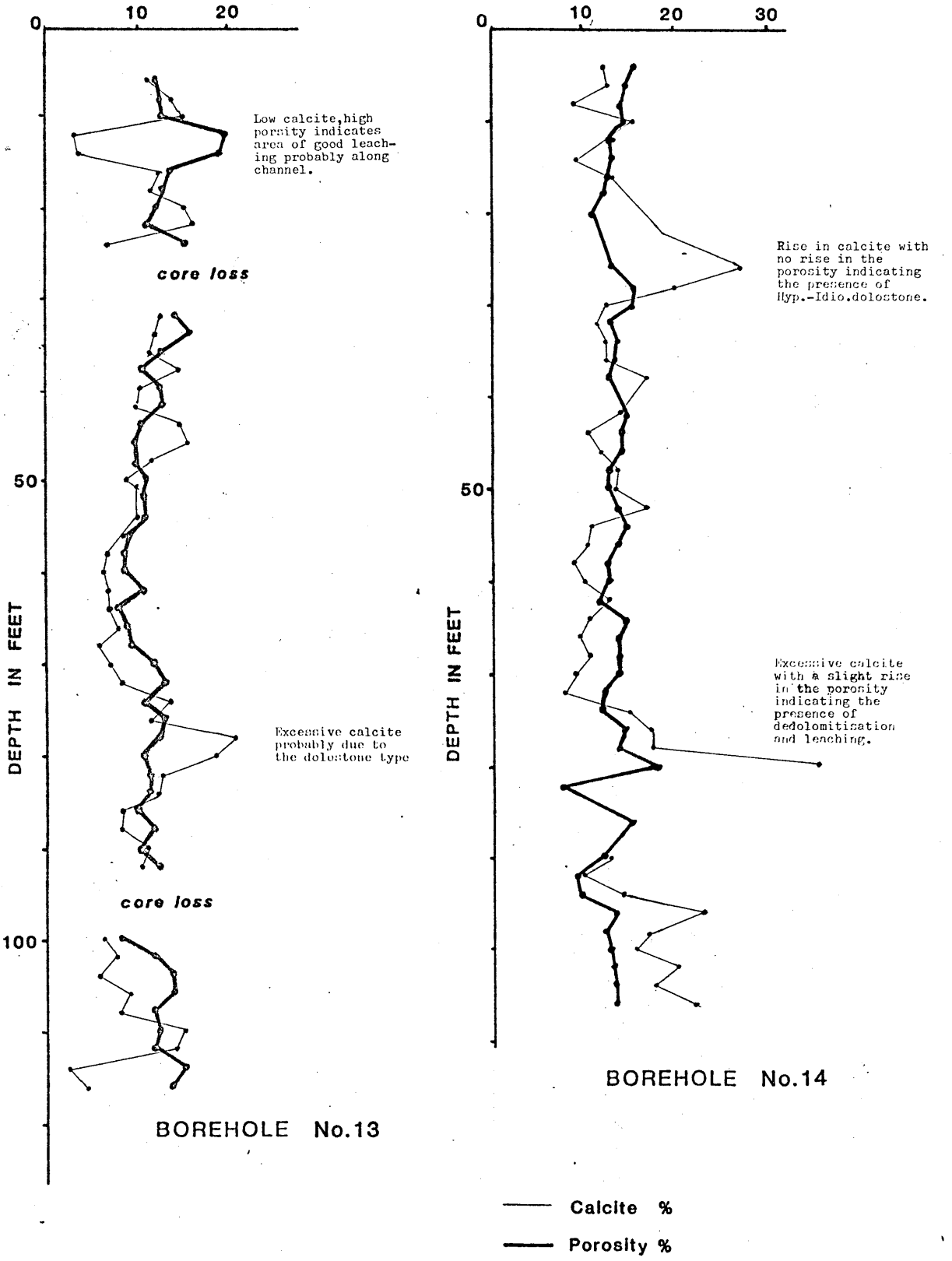


Figure 34 Porosity and calcite logs, plus brief summaries of Harborough Rocks Boreholes Nos. 13 & 14

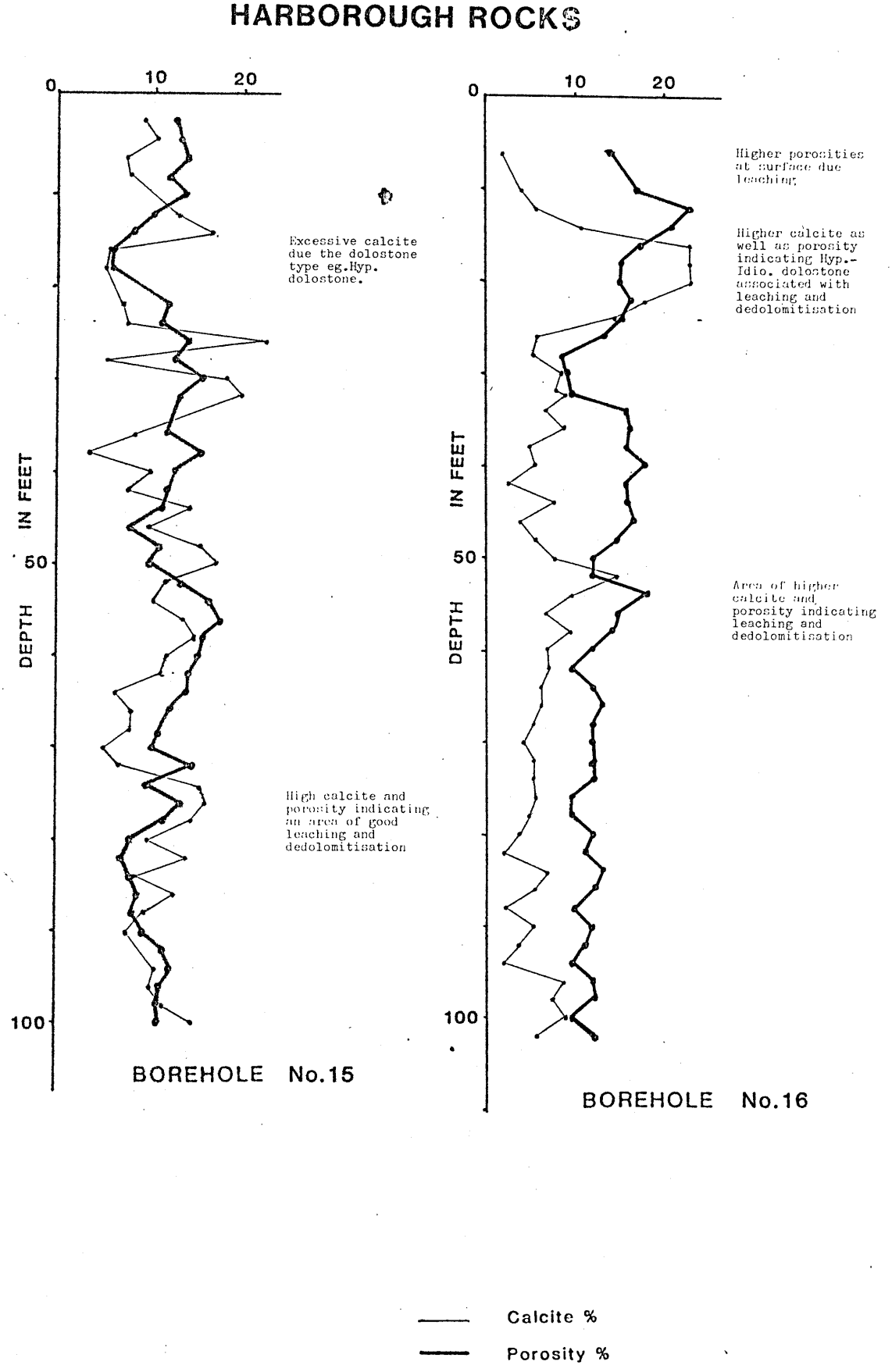


Figure 35 Porosity and calcite logs, plus brief summaries of Harborough Rocks Borcholes Nos. 15 & 16

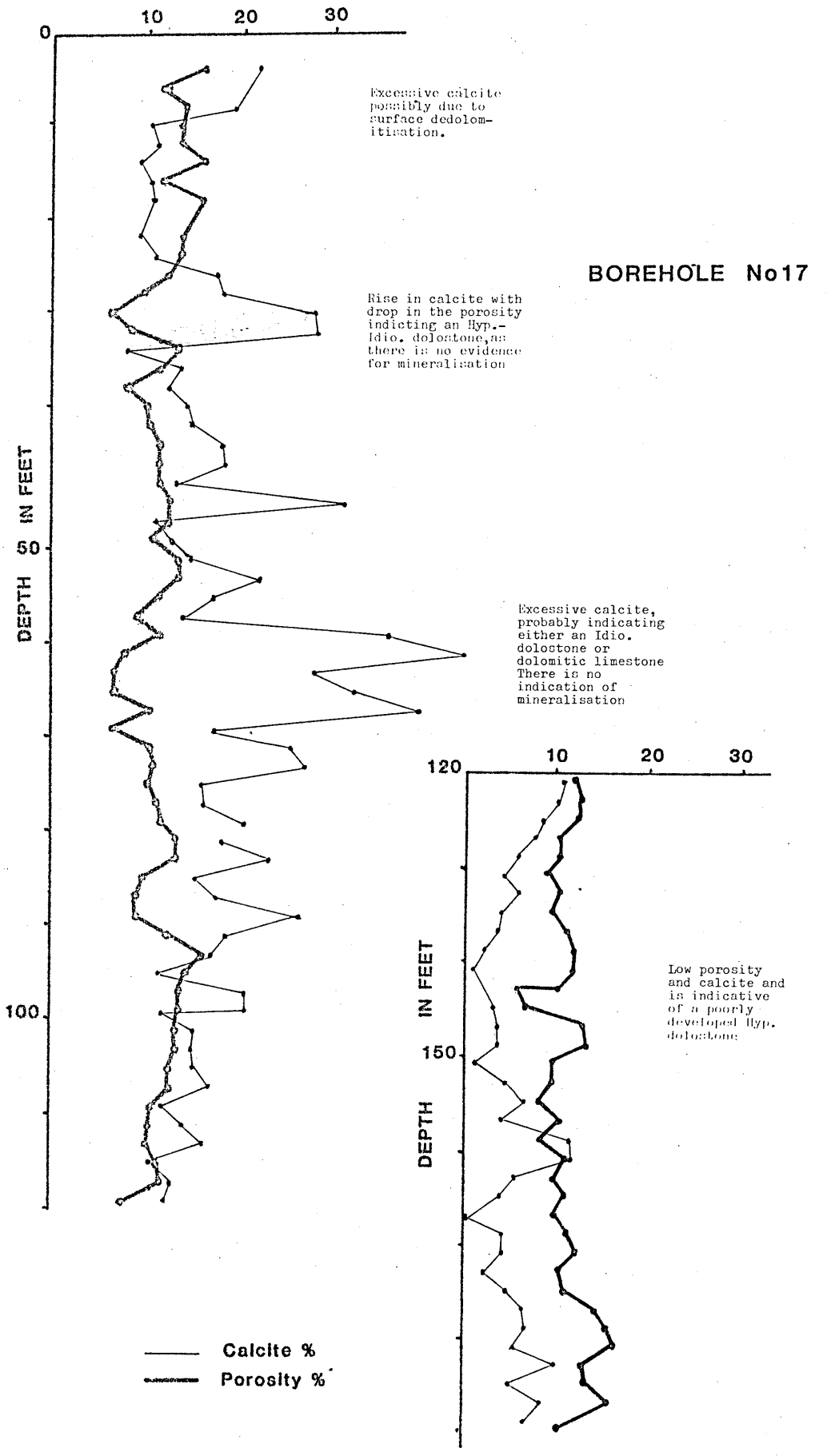


Figure 36 Porosity and calcite log, plus brief summaries of Harborough Rocks No. 17

cannot be seen, due to the sampling interval of 2 feet.

Excessive leaching is marked by a sharp rise in the porosity profile, with quite commonly, a corresponding fall in the calcite profile eg. Bh 13 between 10 and 15 feet (figure 34). Less spectacular examples are seen in many of the boreholes. The areas probably represent the proximity to a karst channelway giving access to dedolomitising and leaching solutions.

No distinction can be made between dedolomitisation around calcite-filled pores or crinoidal pseudomorphs. Certainly, the much higher porosities (eg. Harborough Rocks Section), must represent leaching of dedolomitised crinoidal pseudomorphs. More widespread dedolomitisation, shown to be occurring in the New Harborough Farm and Monyash Boreholes and found to be associated with the areas of leaching, appears to be less common. A possible example of excessive dedolomitisation may be seen in borehole No.3 (120 - 130 feet), where a sharp rise in calcite occurs with an increase in the porosity profile. Sharp rises in the calcite profiles, without a corresponding rise in the porosity profile, which occur throughout the succession, may indicate excessive dedolomitisation.

The very large calcite values probably represent the presence of mineralisation, particularly where a corresponding fall in the porosity profiles occurs. A similar drop in porosity where dedolomitic limestone occurs, due to

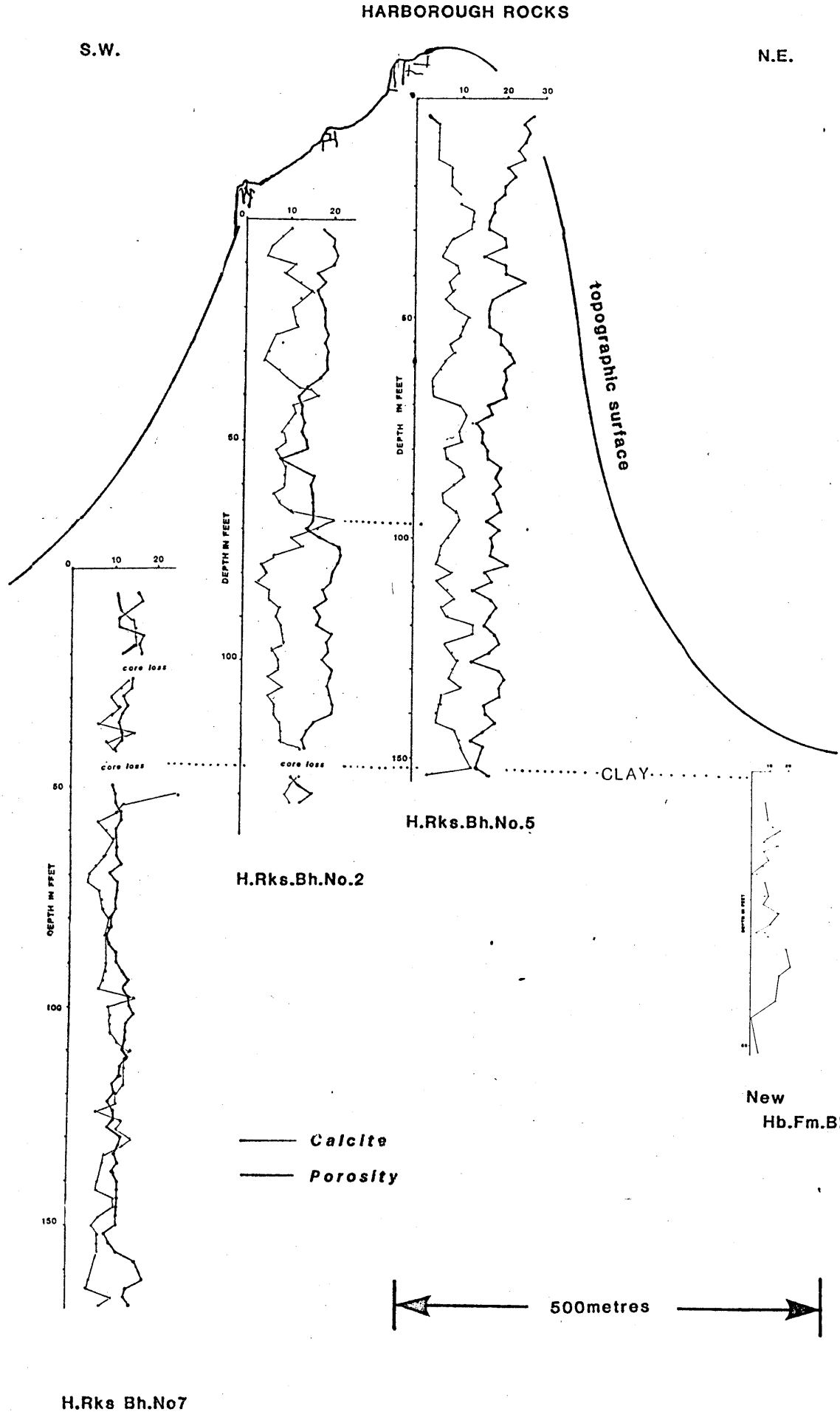


Figure 37 Section through Harborough Rocks(fig.39) showing the relevant boreholes,which indicate an enhancement of the overall porosity towards the top of the Rocks.

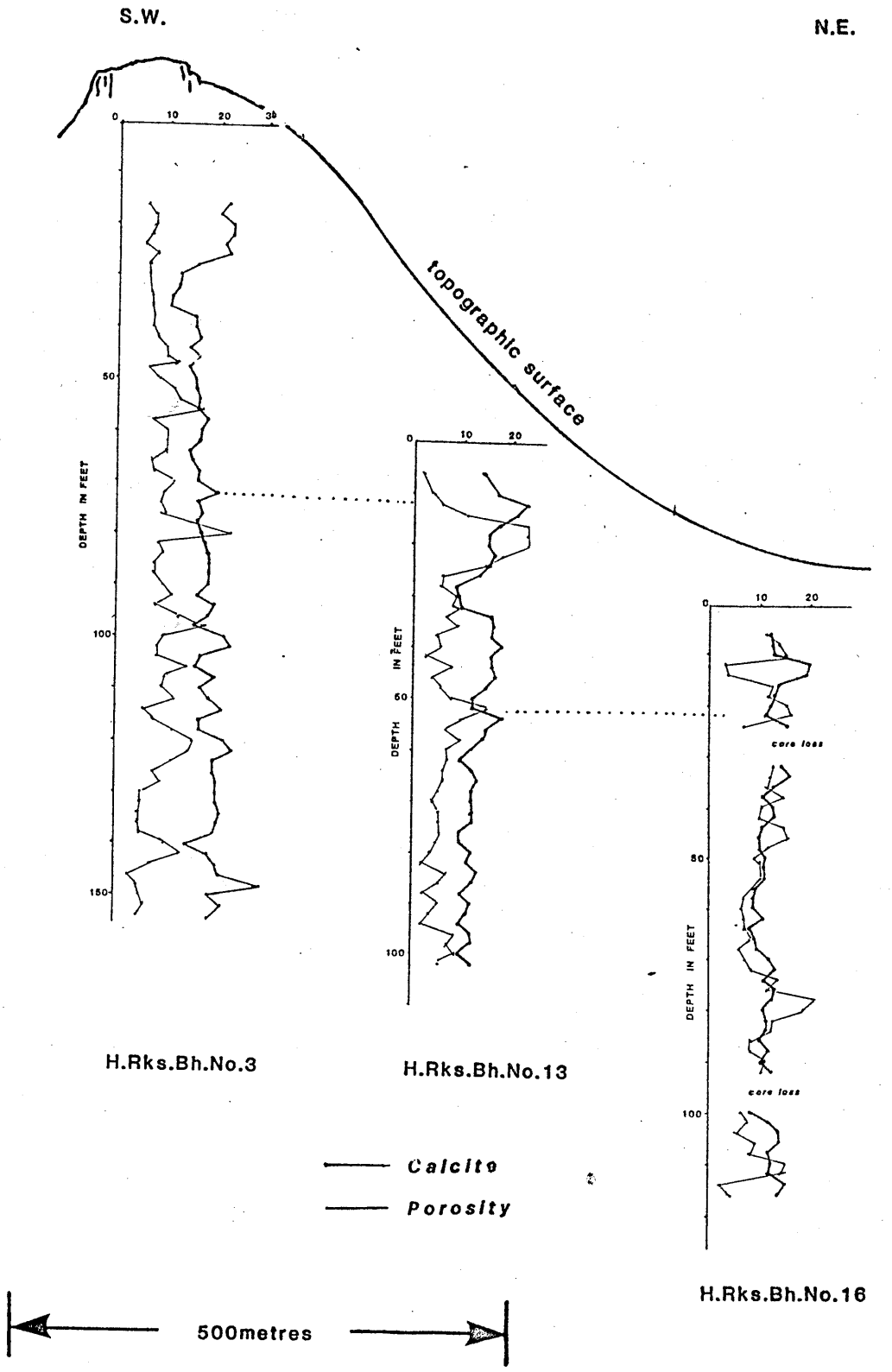


Figure 38 Section through Harborough Rocks(fig.39) showing the relevant boreholes,which indicate an enhancement of the overall porosity towards the top of the Rocks.

mineralisation, can be seen in Traverses 6 and 8 (figures 19 & 21) and the New Harborough Farm Borehole (figure 24).

Clays and shales occur in a number of the boreholes and help in the correlation of different boreholes. Many are associated with a rise in the calcite profile, usually above and below the horizon (as noted in the New Harborough Farm Borehole, (Sect. 5.3.2.). This represents an increase in dedolomitisation from a perched water table above and chemical alteration and incomplete dolomitisation below the clay wayboard. Borehole No.7 (figure 31) shows a corresponding rise in the porosity profile and represents leaching along these channelways.

The majority of the porosity profiles of individual boreholes are quite uniform, although the percentage of porosity varies considerably between comparable boreholes, ranging between 5 and 25 percent. The boreholes which have much higher porosity are seen to be clustered around Harborough Rocks a dolomite tor. The higher porosity is due to greater accessibility of dedolomitising and leaching solutions, causing greater alteration of crinoidal pseudomorphs. The greater alteration can be shown to be due to the position of the boreholes near the top of Harborough Rocks (figures 37 & 38). Many of the boreholes drilled around the top of Harborough Rocks also show a marked increase in porosity near the surface, due to surface seepage (Boreholes 3, 5, 8, 9, and 11), which appears absent in the valley below. Figures 37 & 38 show comparable sections

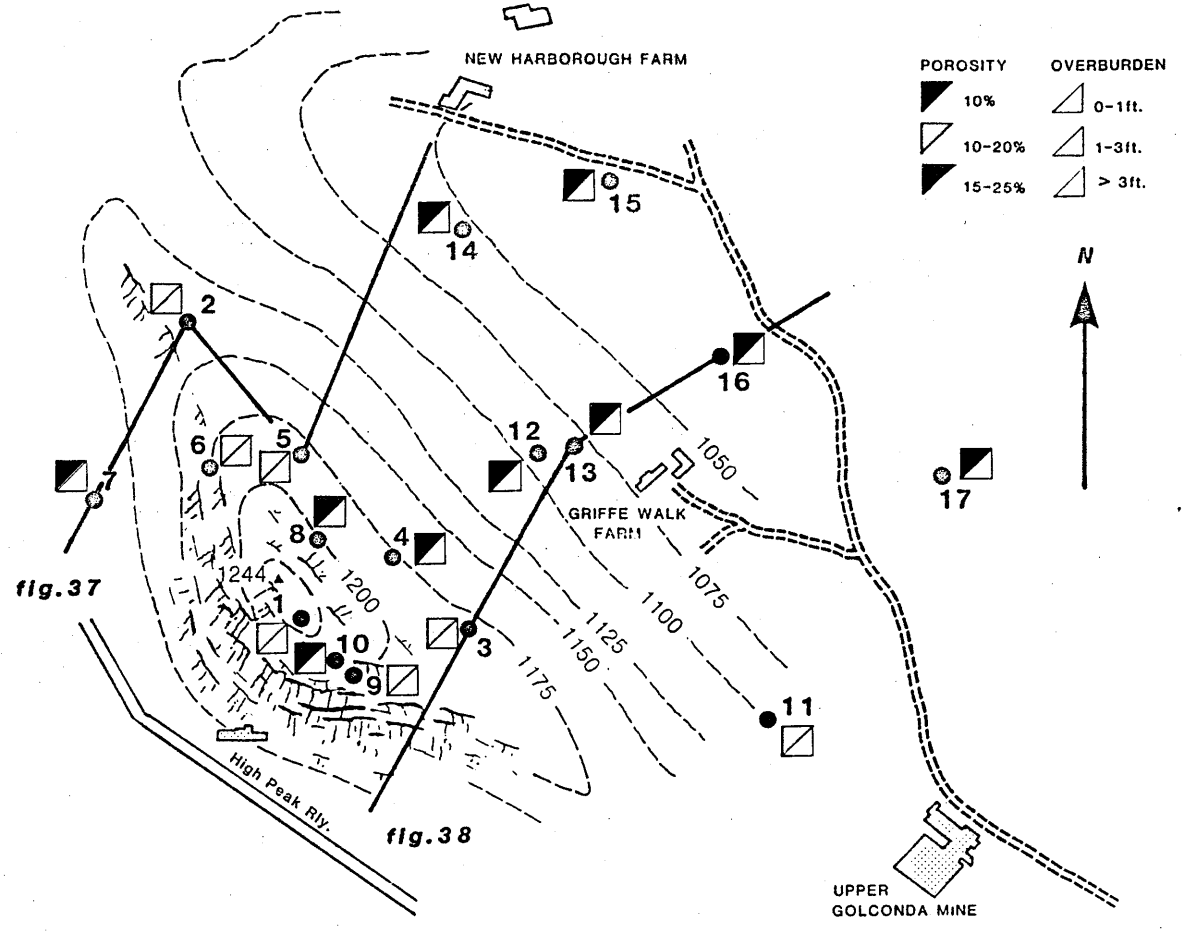


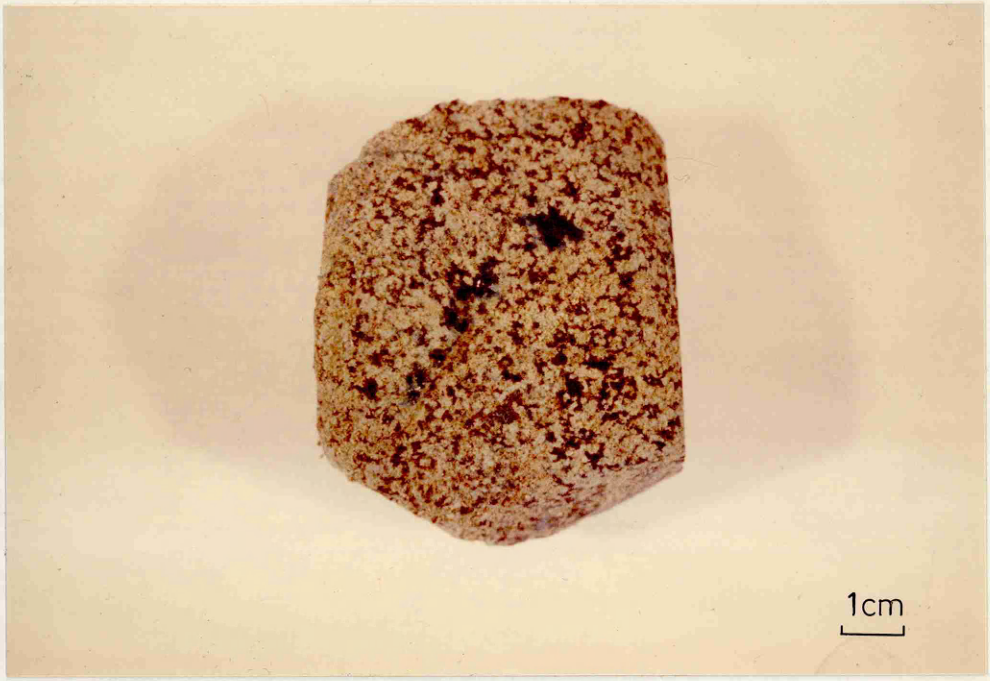
Figure 39 Location map of the boreholes in the Harborough Rocks area, showing the ranges in porosity and overburden, which indicate an enhancement of the porosity towards the

of the dolostones around the Harborough Rocks area, and indicate the enhanced porosity which occurs at the more exposed upper parts of the Rocks and the lower porosity of the dolostones in the valley to the north.

Figure 39 again indicates that the higher porosity boreholes are clustered around the craggy outcrop of Harborough Rocks, but, in addition, indicates the increase in overburden in the valley below, possibly giving a limited amount of protection from surface water. The greater leaching appears to be related to the very exposed nature of the crags. This is thought to be a combination of recent weathering and alteration during the formation of the Harborough Rocks. Harborough Rocks are believed by Ford (1969) to represent a dolomite tor formed by solutional activity after the Miocene uplift, causing the development of sinkholes, of which these tors formed the walls. The onset of the Pleistocene glaciation allowed the removal of debris to expose the tor. Thus the rocks have suffered extensive sub-aerial weathering in Tertiary times. A modern origin for the dedolomitisation is indicated by the enhanced peripheral porosity seen in the Harborough Rocks Section (Section 5.3.4.).

5.4. The Nature of Primary and Secondary Dolostone Porosity

The porosity developed in these dolostones is heavily dependent upon karstification, which has caused much alteration, such as dedolomitisation and leaching. Leaching of pore-filling and dedolomitisation (intercrystalline and pseudomorph) calcite has occurred throughout the succession to give



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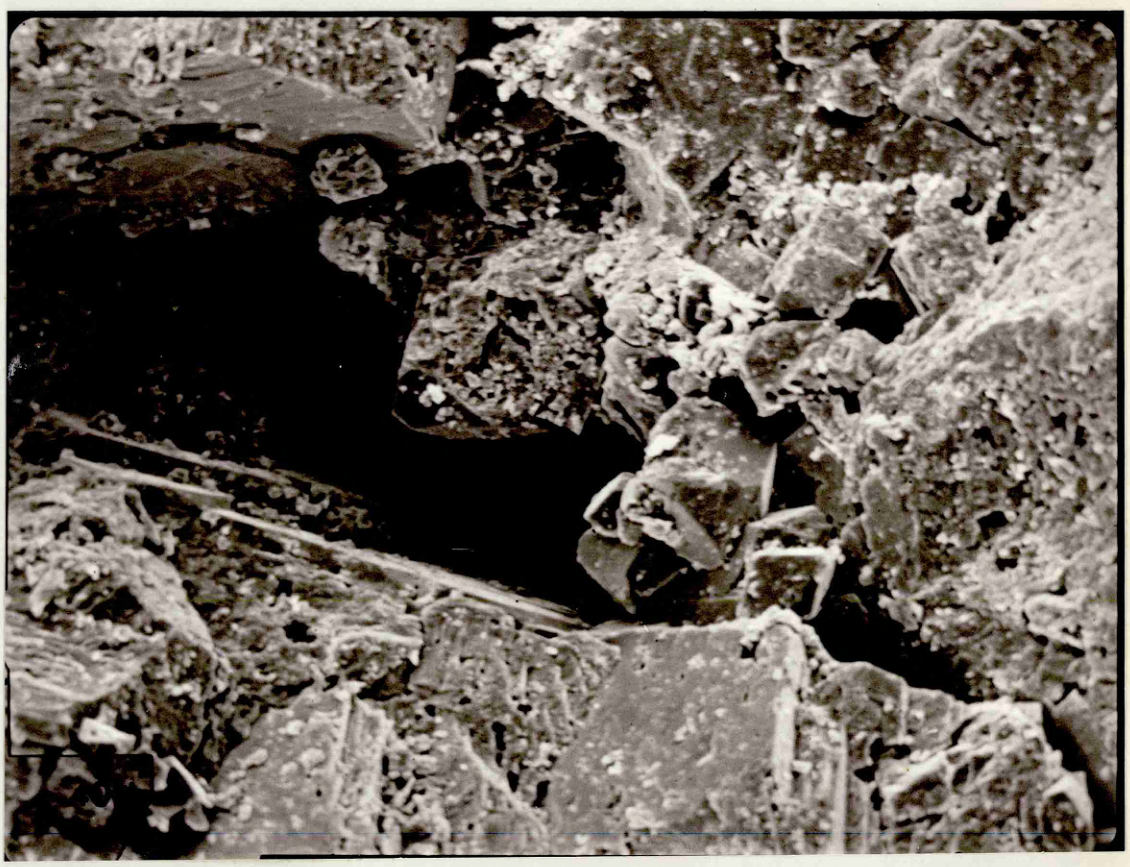


b

Plate 32 (a) Dolostone sample impregnated with a blue resin, the completeness of this impregnation indicates the effectiveness of the method and (b) S.E.M. photograph of a slightly modified polyhedral pore, showing small euhedral dolomite crystals

intercrystalline and mouldic pores and vugs (Choquette and Pray 1970). Localised areas of leaching and dedolomitisation occur at the surface and at depth, adjacent to bedding or jointing. The extent of this alteration depends primarily upon the fabric of the dolostone (Section 4.4.5.).

The dolostone pores and vugs were studied using a Cambridge 600 Scanning Electron Microscope with chip samples and resin casts. The resin impregnations (stained araldite) (pl. 32a) were formed using a simple technique. The samples were evacuated of air in a jar and then completely covered by the resin. The jar was pressurised to the atmosphere and allowed to stand for a few minutes. The samples were removed and the resin allowed to set, before the excess resin was removed by grinding. The dolomite was dissolved in fairly concentrated hydrochloric acid to give the resin casts. The proceedure appears to have worked fairly well.

5.4.1. Intercrystalline pores and Vugs

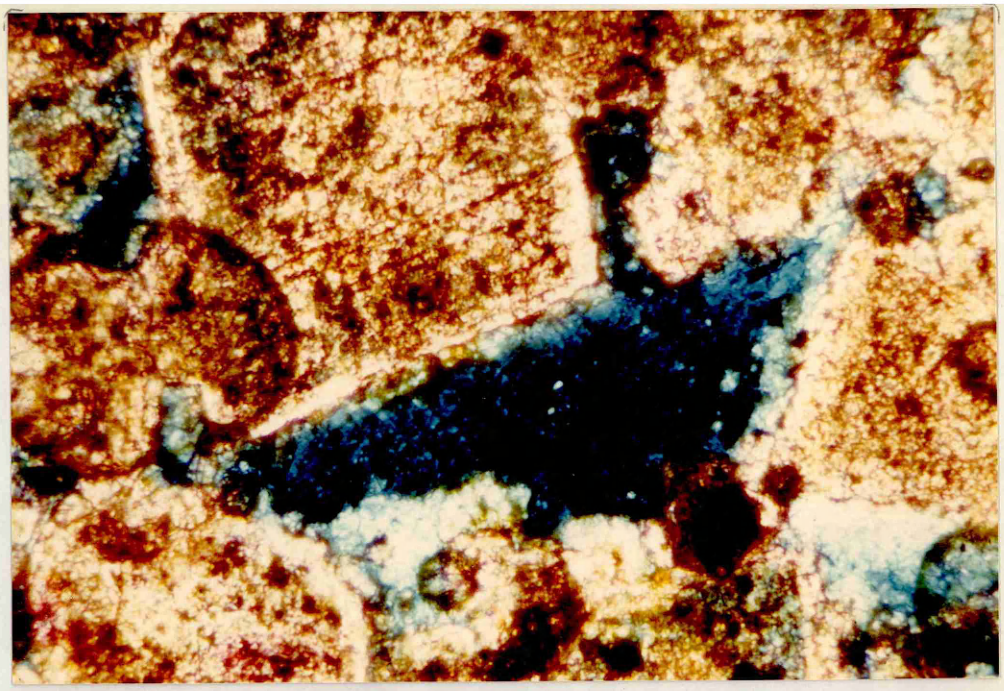
The primary porosity of the dolostones consisted of abundant intercrystalline polyhedral pores (Section 5.2.). These were formed by dolomitic growth around sparry calcite, giving well developed polyhedral pores, ranging in size from 10μm up to 500μm (figure 6). The degree of impingement controlled the type and size of the pores. Where sufficient calcite remained, polyhedral pores developed, often very irregular. Increasing impingement gave smaller tetrahedral and rhombohedral pores. This process of decreasing pore size was also noted by Wardlaw (1976) in pore casts of selected dolostones. The great majority of these pores are formed

due to the presence of crinoidal debris (pl. 32i) and are, in fact mouldic pores, but the fragmentary nature of the debris gives no discernible symmetry. Thus they are termed intercrystalline pores, together with those pores formed as a result of incomplete dolomitisation of non-biological spar (Section 4.4.1.(2). This original porosity is rarely developed due to its occlusion by small euhedra of dolomite, zoning and pore-filling calcite. The pores seen in the weathered dolostones represent regenerated primary pores, modified to different extents by dedolomitisation and leaching to give intercrystalline vugs (pl. 32i).

The dolostone samples show the modified intercrystalline pores and vugs very well (pl. 32i(b)), however a more interesting feature is the presence of dolomite intracrystalline microporosities. These pores range in size from 1μm up to 20μm and vary considerably in their development. Some samples show only a scattered, pitted texture (pl. 33), having circular forms. Others seem to be controlled by the cleavage (pl. 33) and may develop sufficiently to give very irregular forms. These can develop to give a very rotten dolomite, having a dolomicritic appearance, particularly where the inner, less pure, zones of the dolomite are exposed (pl. 33). The outer zones seem to be less altered, the microporosity consisting of scattered pores.

The pores are thought to give the initial access to the rhombs, required to allow dedolomitisation to occur around polyhedral pores. Further dedolomitisation would have led to distinguishable calcite replacement with the typical

a



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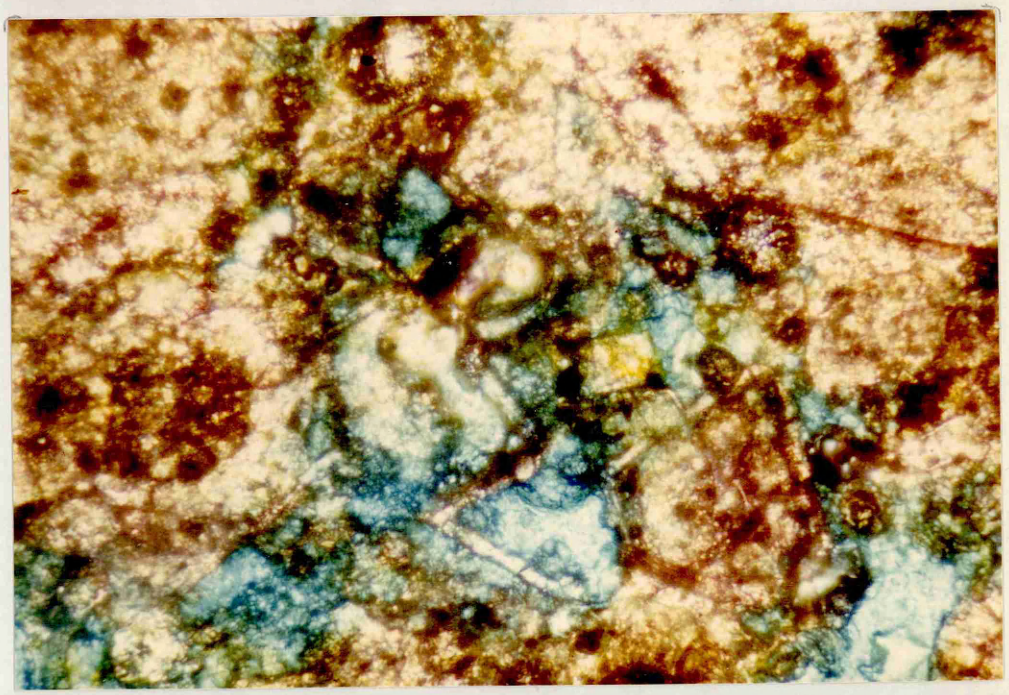

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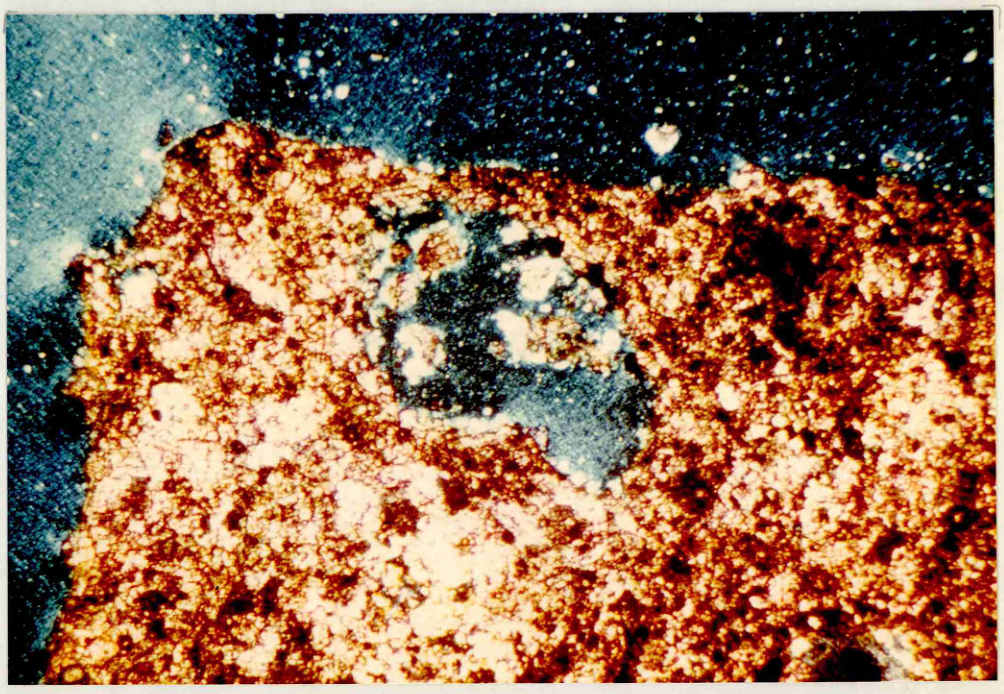
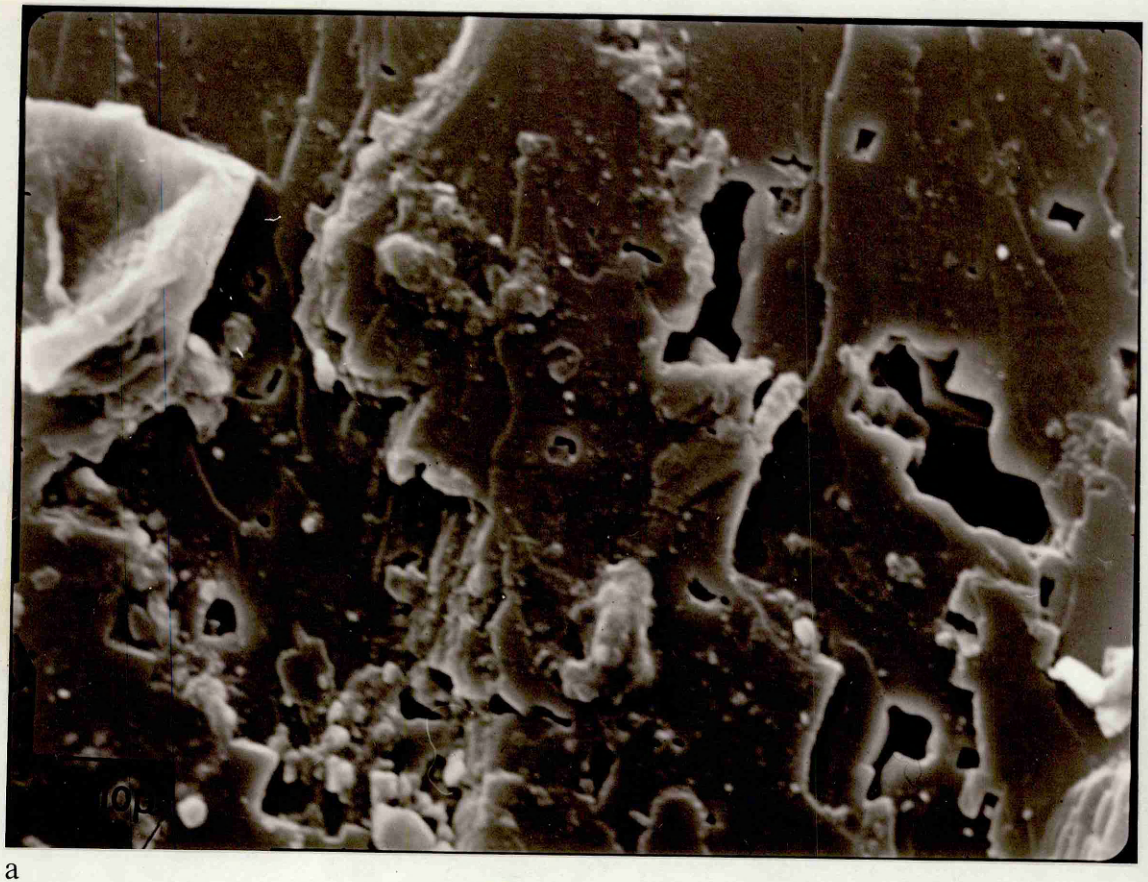


Plate 32i Colour photomicrographs of dolostone porosities(a) polyhedral pore (b) modified polyhedral pore due to dedolomitisation and (c) mouldic pore.



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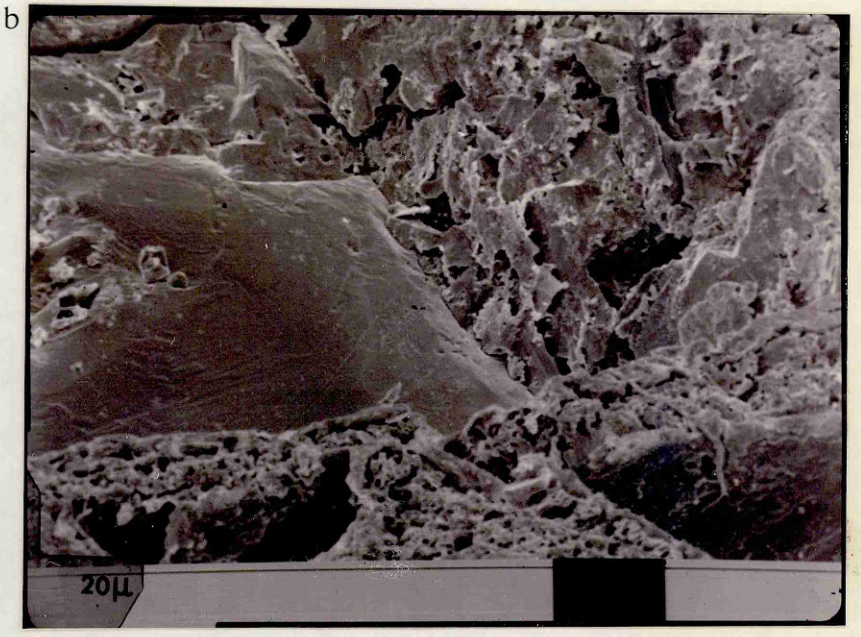


c

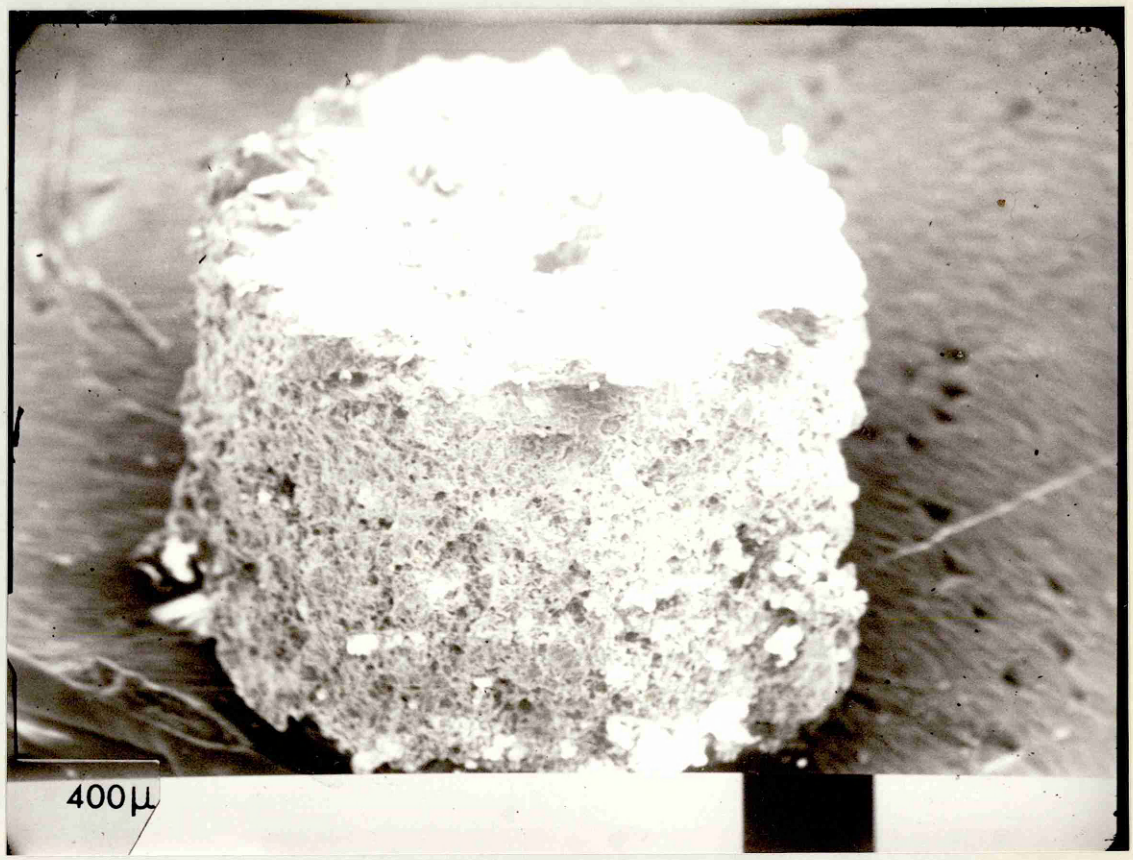
Plate 33 S.E.M. photographs showing intracrystalline porosity (a) both rounded and cleavage controlled intracrystalline porosity (b) acid etched samples showing calcite (smooth crystals) protruding into intracrystalline pores and (c) alteration of the central dolomite leaving an outer rim.

a

b

Plate 34 S.E.M. of dolomite samples showing(a) very rotten dolomite and (b) intracrystalline porosity in large anhedral pseudo-

a



b

Plate 35 Resin casts obtained by the leaching of impregnated dolostones (a) showing a good replication of a polyhedral pore, a little modified and (b) cast of a mouldic pore.

poikilotopic calcite and dolomite remnants (Section 4.4.5). Samples that were slightly leached with dilute acetic acid to indicate the dedolomitisation textures, show these micropores in the exposed dolomite faces (pl.33), and some examples show calcite protruding into these pores (pl.33). The circular nature of the initial pores (although later modified) may suggest a fluid inclusion origin, although this is not proven. Alternatively they may represent calcite remnants enclosed within the dolostone (Evamy, 1967), but this seems unlikely due to the very pure nature of the outer zoning and lack of high Ca^{2+} analyses found during the microprobe analysis (Table VI). The large dolomite pseudomorphs also show a similar texture (pl. 34), with the possible dolomicrite also visible. Dolomicrites have been noted earlier in connection with these pseudomorphs (Sect. 4.4.5.), and are thought to be primarily caused by stress. This evidence may suggest that dolomicritisation is also related to the dedolomitisation process. However, this would not explain, in some samples, the absence of calcite in many dolomicritised pseudomorphs.

The resin casts taken from a surface sample showing dedolomitisation and leaching, indicate that the intercrystalline pores of the original dolostone are commonly regenerated, although slightly modified, by the dedolomitisation (pl.35). Further dedolomitisation has caused much more irregular vugs to develop, further modifying the original porosity. It must be appreciated that both porosity types occur within the same sample, due to the accessibility of different areas of calcite to aggressive solutions.

5.4.2. Mouldic Pores and Vugs

The mouldic pores and vugs are splendidly displayed in the Hoptonwood"Group"at Harborough Rocks. It is difficult to distinguish primary and secondary moulds where calcite or remnant rims are absent (Sect. 4.4.5.). Certainly, where single large anhedral, poikilotopic calcite crystals are present, which include many dolomite remnants (pl. 26), or an optically continuous rim of dolomite remains, a dedolomitisation origin is suggested. The moulds of Harborough Rocks are thought mainly to be secondary, from the scattered evidence of calcite and rims. The pores and vugs range in size from 500µm up to 20mm and are usually cylindrical, having a fairly good symmetry and commonly showing the presence of a central column of dolomite, representing the dolomitised mud infill of the central canal. The resin casts, due to the irregularity of dedolomitisation show little surface texture, apart from segment junctions. Some moulds occassionally show a surface ornamentation. This may suggest a primary origin for the mould, as these have not been modified by dedolomitisation. Mouldic vugs have been shown to be very important throughout the dolostones as a provider of porosity due to their greater susceptibility to dedolomitisation and leaching.

5.5. Conclusion

The evolution of the porosity in these dolostones has gone through a number of stages. The model presented here is partly theoretical and partly observed, (figure 40). The originally high porosities of the unconsolidated carbonates

were destroyed by relatively early diagenesis to give a quite low porosity limestone. Dolomitisation by a volume for volume replacement produced variable porosities due to selectivity of dolomitisation. Finally, sub-aerial weathering throughout geological time, although much does appear to have formed more recently, has begun to regenerate the primary dolostone porosity by leaching of the pore-filling calcite. In many cases the pores have become modified to varying extents, by dedolomitisation to give intercrystalline vugs. Dedolomitisation of dolomite crinoid pseudomorphs, occurring at the surface, allows greater solution giving mouldic vugs. A very similar vacillatory sequence of porosity development was described by Freeman (1969) in the Muschelkalk carbonates of eastern Spain.

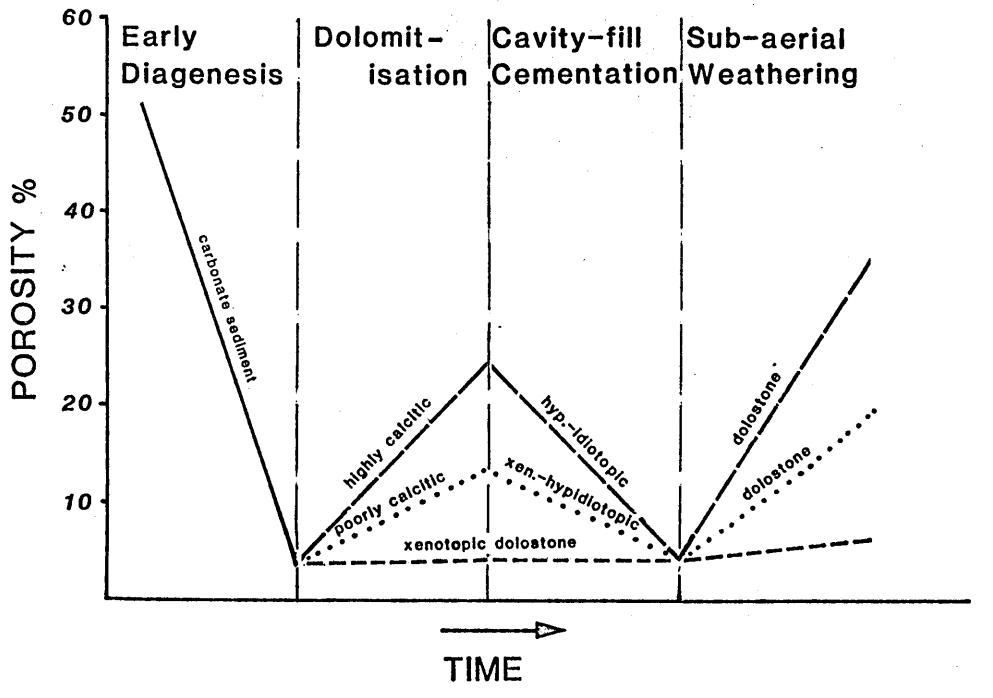


Figure 40 The vacillatory nature of the porosity development in the Wirksworth Dolostone.

Therefore, the porosity in the dolostones of the Wirksworth area is primarily a consequence of sub-aerial weathering, although the extent to which it develops is strongly influenced by the fabric of the original dolostone. Results have shown that excess leaching of the dolostone occurs at the surface and at depth in the succession along features such as bedding, jointing, caves, fractures and possibly unconformities, where an ample supply of aggressive water, charged with carbon dioxide from the atmosphere and soil, is available to cause extensive dedolomitisation and leaching. The degree of alteration depends on the type of dolostone present. The xenotopic dolostones, due to their lack of original porosity, are not affected to any great extent, however the xenotopic-hypidiotopic and idiotopic dolostones, where these occur adjacent to karst channels, are extensively altered, the degree of alteration depends on the amount of calcite. Highly calcitic dolostones in this situation will promote extensive dedolomitisation and leaching to give a very good porosity, occasionally leaching to a very rotten dolostone, which may become eroded to cause widening of the karst channel. Less calcite xenotopic-hypidiotopic dolostones give a very porous coherent dolostone. Metwalli and El-Haby (1975) also attributed the increase in porosity of the Alamein Dolostone in the Middle East to the leaching of dedolomitisation calcite. Away from these areas of excess leaching some dedolomitisation and leaching occurs, much of which appears to be caused by the alteration of crinoidal pseudomorphs, giving the dolostones a quite high overall porosity.

In the more exposed areas, such as Harborough Rocks, greater overall porosities develop, relative to the more sheltered dolostones in the valley to the north. These and the enhanced porosities of the shallow boreholes may be related to the proximity of the weathering surface, because below 40 metres in the Ryder Point Boreholes the surface enhanced porosities drop markedly, reflecting the ineffectiveness of this karstification at depth. The surface enhancement of porosity may be influenced to some extent by the amount of overburden. The overall porosity seems to decrease under greater thicknesses of overburden. The enhancement at Harborough Rocks, both below and on the face, indicates that modern weathering has played a significant role in the karst development seen today.

The extent of karstification in the succession will depend upon a number of factors such as lithology, mineralogy, relief, climate, tectonics and time. In this study the most prominent karst features are solution-widened jointing and caves. The amount of porosity given by these karst features has been found to be similar to other areas of karstified dolostone, such as in South Wales - giving values of 2 percent in the Hoptonwood "Group" (High Peak Railway) and 2 percent in the Matlock "Group" (Hopton Tunnel). It is suggested, but not confirmed by this study, that the dolostones do appear much more weathered and seemingly give better development of karst features than comparable limestones. This may be related to their more brittle nature (figure 12), allowing

many more joints develop and thus a greater access for aggressive waters into the succession. These porosities, due to karstification, almost certainly decrease with depth. Even within the depth of a quarry the solution-widened joints close considerably (plate 1). This is also suggested by the results of the Ryder Point Borehole.

C H A P T E R S I X

An Account of the Palaeokarstification and Mineralisation Associated with the Limestones and Dolostones of the Wirksworth Area.

6.1. Palaeokarstification

The Lower Carboniferous Limestone sucession of the Derbyshire Dome can be shown to have been affected by at least four periods of karstification. These periods of sub-aerial exposure account for much of the diagenesis of the limestone and have exerted much influence upon dolomitisation (Section 4.4.1), mineralisation and, more recently, the dedolomitisation and enhanced porosities (Section 5.3). However, as discussed in Chapter V, some of the dedolomitisation and leaching may be related to any of these earlier phases of karstification.

6.1.1. Intra - Lower Carboniferous Palaeokarst

Walkden (1974) has shown that the clay wayboards, commonly associated with the Lower Carboniferous Limestone succession of Derbyshire, examples of which can be seen in Hoptonwood Quarry (pl. 36), represent sub-aerial deposits of volcanic dust. These commonly have an irregular base (pl. 36), which Walkden has shown to represent minor karstification developed below these palaeosol horizons. The evidence for these irregular bases being a consequence of palaeokarstification, and not recent solution, is given as;

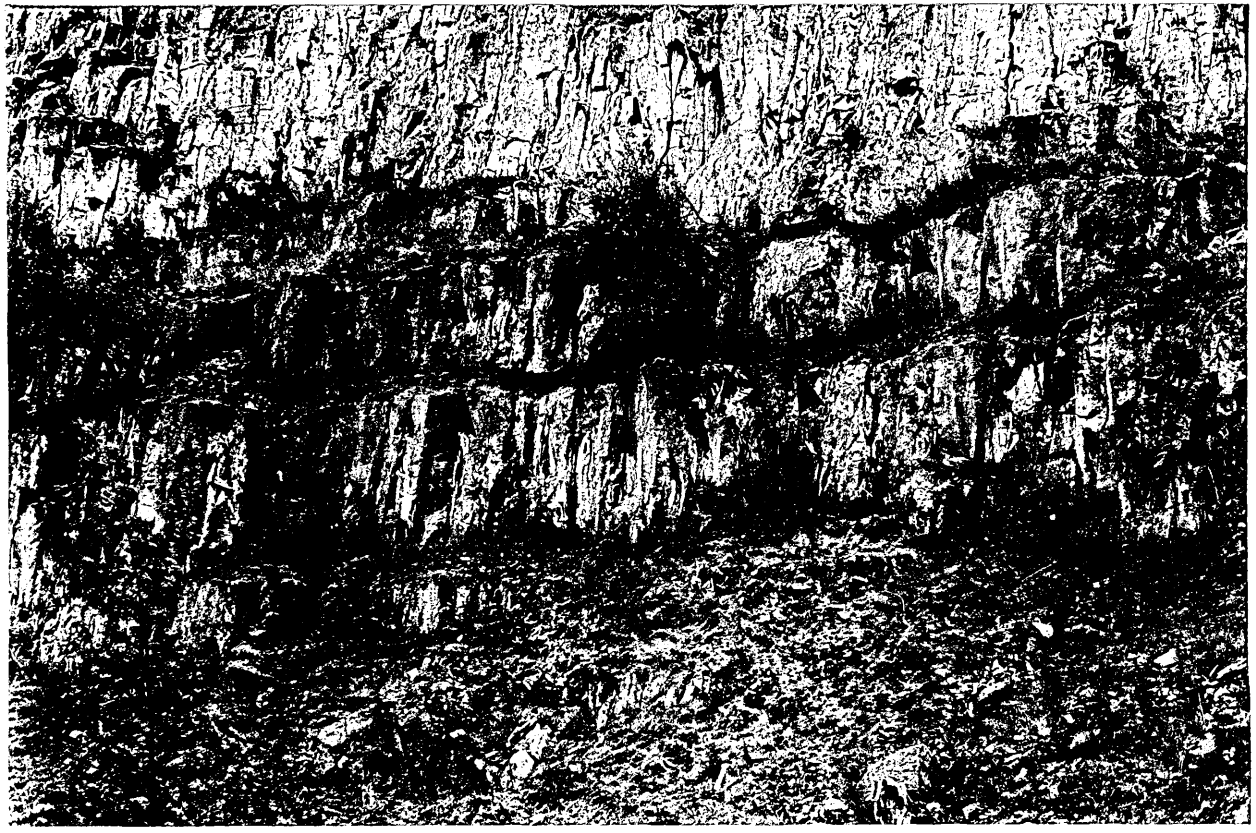


Plate 36 Hoptonwood Quarry, showing a distinct clay wayboard and the characteristic irregular base.

(1) the clays in these pits when freshly exposed are found to be dry and hard, even though the upper layers are wet; (2) the morphology of the mammillated surfaces bears no relationship to jointing and (3) the axes of the pits lie perpendicular to the bedding and not the present-day horizontal. Somerville (1979) has recently found similar palaeokarstification in the limestones of North Wales. Thus, it seems likely that throughout Lower Carboniferous times, sporadic sub-aerial exposure of limestone occurred. This allowed the development of the karst features but more importantly allowed the stabilisation and cementation of the carbonate sediments (Sect. 2.3.) giving low magnesium calcite which is so typical of the limestones.

6.1.2. Pre-Namurian Palaeokarst

Towards the end of Lower Carboniferous times uplift and appreciable erosion gave a relief to the limestones, estimated to be 500ft. This was associated with extensive karstification, which Ford (1964) estimates has being operative for as much as a million years. No direct evidence for this unconformity and karstification can be found in the study area. The general form of the unconformity was described by Hudson (1930) in upper Dovedale and further comment made by Ford (1952) in the Castleton area. At Treak Cliff near Castleton, there are examples of swallow holes filled by limestone boulders bound in a matrix of black shales. The shale matrix represents the overlying

Edale Shales (Ford, 1952). This episode of karstification, although no evidence exists of it in the Wirksworth area, may have provided the necessary access for the dolomitising fluids (Section 7.3.2(b)).

6.1.3. Permo - Triassic Palaeokarst

Folding and faulting at the end of Carboniferous times caused uplift, and erosion of the Upper and Middle Carboniferous sediments during the Permo - Triassic in the Derbyshire region. Little is known of the early Permian phase of exposure of the Carboniferous Limestones but chert and limestone conglomerates found within the Permian beds of Warwickshire suggest that the Lower Carboniferous Limestone was undergoing erosion at this time. By Triassic time, extensive exposure had occurred, as chert pebbles similar to the cherts in the Derbyshire Lower Carboniferous Limestones are commonly found in the Bunter Pebble Beds around Derby.

In the Wirksworth area, Walsh et al., (1972) have shown that the Lower Carboniferous Limestone was covered by a thin veneer of Namurian shale (c. 21m), as late as the Neogene, although they do not rule out the possibility of localised limestone exposures which allow the dolomitisation of the limestone (Ford, 1967). The presence of Namurian shale and the uncovering of the Lower Carboniferous Limestone in more recent times was also suggested by Pitty (1968). This was based upon rates of solution and drainage patterns

(Sect. 7.3.1.).In the Wirksworth area, Ford (1968) believed that this exposure of the Lower Carboniferous beneath an extension of the Zechstein Sea allowed the development of dolostones due to the seepage of magnesium-enriched evaporitic brines (Sect. 7.3.1.). Some doubt exists as to whether the chemistry of these dolostones support such an origin (Sect 7.3.1). If we assume an earlier origin for the dolomitisation, whether in the Carboniferous (Sect. 7.3.2) or the Permian, the exposure of the limestone during the Triassic clearly accounts for the karstification associated with the dolostone base which has formed a quite extensive cave system. This period of karstification appears to have had a profound affect upon the distribution of mineralisation, as the mineral deposits are invariably associated with this porosity (Sect. 6.2.).

6.1.4. Pre - Glacial Palaeokarst

The remainder of the Mesozoic times in the Derbyshire region is represented by a great gap in geological knowledge, but it is deduced from surrounding outcrops that the area was covered by Jurassic and Cretaceous sediments which have only been removed during the last 70 million years. The post Mesozoic period of erosion has been associated with extensive karstification, to which much of the late diagenesis of the dolostone i.e. dedolomitisation and leaching is attributed.

Pre-glacial karstification is clearly evident

in the Wirksworth area, in the numerous "Pocket Deposits" e.g. Bees Nest Pit (ref. 238547). Over sixty of these deposits are known, scattered around this southern portion of the Dome (fig. 41) and are commonly associated with the 900 - 1100ft. erosional surface (Kent, 1957).

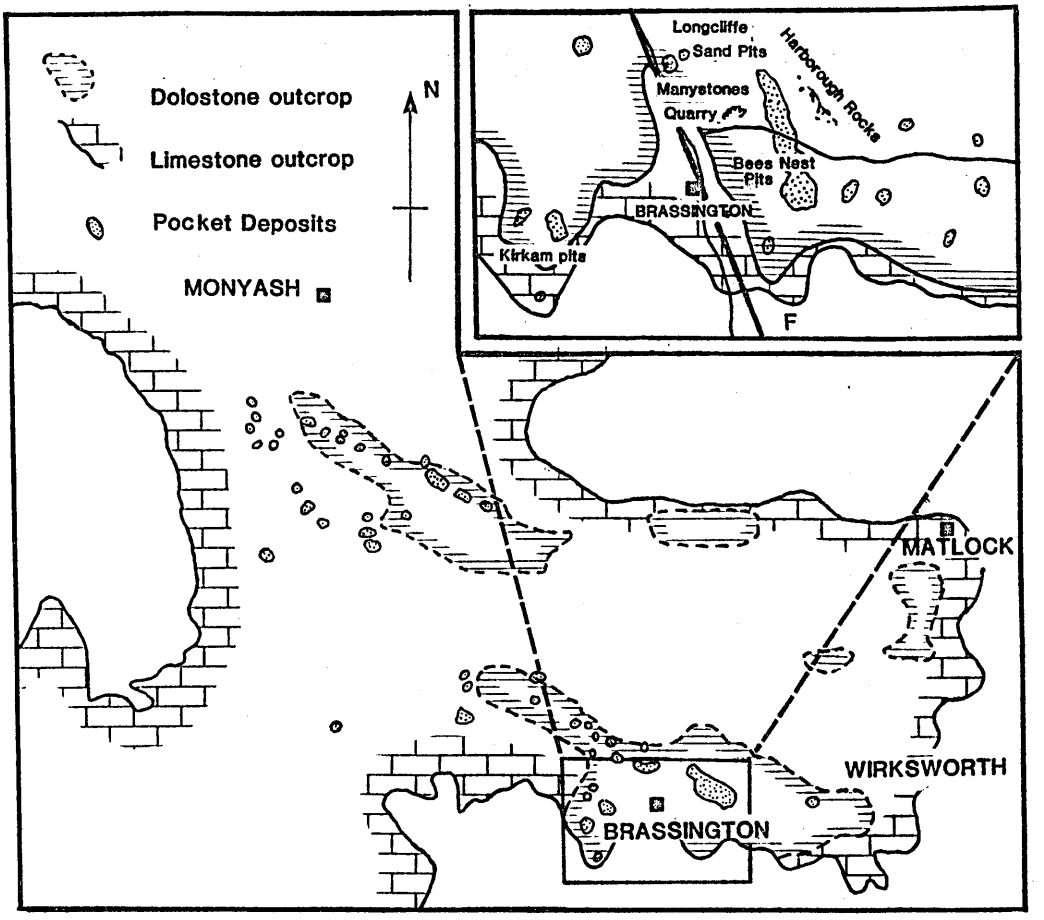


Figure 41 A map of the southern part of the Derbyshire Dome, showing the locations of the numerous pocket deposits particularly around the Brassington area.

These consist of steep-sided pits which are infilled with sand, gravel and clay, commonly showing collapse structures. Hughes (1952), Kent (1957) and Yorke (1961) believed these deposits to have a Triassic age, due to similarities in lithology sediment size distributions and heavy mineral assemblages to the Bunter Pebble Beds and Keuper Marls.

These pocket deposits are thought to be formed either by the filling of swallow holes in the Lower Carboniferous Limestone, and later collapsing due to the action of groundwater (Hughes and Yorke) or recent collapse of overlying Triassic sediments into swallow holes, formed by karstification in the Mesozoic or early Tertiary. The uppermost grey clays (Kenslow clays of Walsh et al., 1972) are accepted by these authors to be formed as lacustrine deposits, during the Tertiary. A fact confirmed by Ford and King (1965) from palaeobotanical studies. Recently the conformable nature of the Kenslow Clays (Kenslow Member) with the underlying red and green clays (Bees Nest Member) and sands and gravels (Kirkham Member), which comprise the Brassington Formation (Walsh et al., 1972), has led the deposits to be recognised as Neogene in age. As suggested by Ford and King (1968) and recently proven by Walsh et al., (1972), the Kirkham Sands, although probably derived from the Keuper Sandstone, show significant difference in their heavy mineral assemblages. Similarly, none of the characteristic clay minerals of the Keuper Marls are found in the Brassington Formation. Thus the Pocket Deposits are thought to have been deposited during early Pliocene, the sediments being supplied from the reworking of the Triassic. After deposition of the Brassington Formation upon a shale covered limestone outcrop, Walsh et al., (1972) suggest that uplift in the Mid-Pliocene caused swallow holes to develop. The continuing

cavernisation of the limestone during late Pliocene times caused the collapse of the Brassington Formation, to give the characteristic slump structures found in these deposits. The probable origin of this cavernisation below the Brassington Formation, is thought by Ford and King (1968) to be related to mineralisation and solution which has occurred at the base of the dolostone (fig. 10). Extensive development of the caves, by leaching along the base of the dolostone, may provide the necessary weakness for the formation of these Pocket- Deposits. The collapse of such caverns, together with mass wastage during exposures during the Pleistocene are believed by Ford (1969) to have developed the common dolomite features e.g. Harborough Rocks (pl. 37).

Plate 37 Harborough Rocks; a dolomite tor

During the Pleistocene, the much higher water table allowed continual sedimentation in the cave system in the less active parts of the phreatic zone developed mainly in Mesozoic and Tertiary times, giving a typical buried karst. Good examples of this can be seen at Masson Hill Quarry, near Matlock, just north of the study area. Although some evidence of this sedimentation can be seen in the Wirksworth area e.g. High Peak Quarry and an adjacent railway cutting.

In conclusion, it has been shown that the limestone succession of the Derbyshire Dome has been sporadically exposed to subaerial weathering and karstification since early Carboniferous times. The stabilisation, induration dolomitisation, cementation, dedolomitisation and leaching of these carbonates cannot be ascribed to a particular period of subaerial exposure. In particular the enhanced porosities found in the dolostones of this study have been formed as a consequence of dedolomitisation and leaching being associated with karstification. As discussed in Chapters IV and V, dedolomitisation and leaching may have occurred,to a certain extent, during an earlier period of exposure, although geochemical evidence does show these processes to be widespread in the present-day weathering profile.

6.2 Lead - Zinc Mineralisation

The Carboniferous Massif of the Derbyshire Dome is traversed by hundreds of mineral veins containing galena, sphalerite, fluorite, baryte and calcite, as well as a number of less economically important minerals. The veins have been worked since Roman times, chiefly for lead, although more recently fluorite and baryte have become important. After reaching it's peak in the eighteenth century the industry dwindled in importance, until in the last part of the nineteenth century it had almost died. The numerous old mine workings and shafts serve as a memorial and a stark reminder to this glorious past, throughout much of the Derbyshire Dome.

The veins have been classified by the Derbyshire miners as rakes (fault-filling), scrins (small fissure fillings), flats (horizontal ore bodies) and pipes (similar to flats

Plate 38 Coarse calcite crystals filling former caves along the dolostone-limestone transition at Manystones Quarry.

only the length far exceeds the width). Rakes and scrins are almost all developed along faults and small joints, whereas the flats and pipes have more widespread occurrences. The major occurrences of flats and pipes in Derbyshire were given by Ford (1967) as being (a) below the Edale Shale cover eg. Treak Cliff, Castleton (b) below and resting upon impervious toadstones (lavas) eg. Mill Close Mine, (c) occurring at the base of the porous dolomitised limestone eg. Golconda Mine and (d) within pre-existing karst.

In the Wirksworth area the lead-zinc mineralisation occurs as stratiform bodies in flats and pipes, occurring at the base of the dolostone. The minerals have been deposited within solution cavities, developed along the undulating base of the dolostone (Sect. 6.1.3) which are thought to be produced either by subaerial weathering prior to mineralisation or as King (1966) suggested by an early phase of the mineralisation. Examples of the mineralisation can only be studied in the dolostone area at Manystones and High Peak Quarries, due to the closure of Golconda Mine (ref.249532) in 1964. At Manystones and High Peak Quarry typical examples of the mineralisation can be found. The mineralisation consists of a coarse calcite gangue showing little galena or sphalerite, infilling quite large solution cavities (pl. 38). The mineralisation appears to affect the underlying limestone very little, however dolostone is quite markedly altered where it abuts mineralisation.

of any significance. As noted in Section 4.4.5 mineralisation causes total dedolomitisation of the dolostone to a very coarsely crystalline, low-magnesium calcite. The evidence of a former dolostone is given by the numerous ghost-like textures in the calcite (pl. 21F). A more localised feature of the mineralisation may be the remobilisation of dolomite around isolated mineral-filled vugs. It is felt that this may supply the solution which has caused the outer zoning seen in many dolostone samples (Section 4.3.3).

The largest deposit, and most commonly described, is that of Golconda mine. Again, the mineralisation is found only associated with the dissolution-affected dolostone base. The dominant minerals present are galena and barytes, with sphalerite, chalcopyrite and chalcocite present as traces, but having become oxidised to haemimorphite, aurichalcite, a little smithsonite and hydrozincite. The ore body is essentially stratiform, with many associations such as layered ore, cavity lining, collapse breccias and cavity lining, later cavity lining, metasomatic replacement, secondary oxidation and placer deposits (Ford and King 1965).

6.2.1 Origin of the Mineralisation

The age of the mineralisation has been given by Moorbath (1961) as being 180 ± 40m years, i.e. Late Triassic to early Jurassic. The origin of the mineralising fluids is less

certain. Wedd and Drabble (1908) noted a thermal zoning of the gangue minerals and they suggest that higher temperature fluorite is more common in the east. Towards the west lower temperature barytes and calcite are more important. This has led many writers to suggest that the hydrothermal fluids originated to the east.

The origin of the fluids has also been discussed by Dunham (1952), Ford and King (1965), King (1966) and Ford (1967) and two major ideas predominate; the first is that the minerals came from groundwater, which was mobilised by a granite to the east. Unfortunately no borehole, gravity or aeromagnetic information has confirmed its presence (Ford 1968). The second is that the fluids represent a remobilisation of mineral-rich salts found within the Permo-Triassic sediments. In the late Triassic remobilisation of the mineral salts in the vadose zone, could have resulted in a concentration of minerals in the deep water table, thus allowing mineralisation of any convenient depository, such as a karstified limestone. The minerals in the Permo-Triassic sediments are thought to have originated from hydrothermal springs discharging into the Zechstein Sea (Dunham 1952). The geochemical analysis of the gangue calcite occurring in the study area has provided little information on the origin of the mineralisation fluids. The rare earth element patterns (fig. 50) indicate that much of the carbonate material has been supplied by the dissolution of the limestone and dolostone (Section 7.2.6.). However,

the rare earth concentrations are much higher in the mineralisation calcite, compared to normal limestone. Parekh et al. (1977) describe calcite associated with lead-zinc mineralisation with very similar patterns and concentrations (fig. 50), and believe these to have been formed by dissolution and remobilisation of local limestone by granitic magma. Whether the remobliisation of mineral salts from the Permo-Triassic could produce a similar concentration of rare earths is not known. In relation to the limestone the chemistry of the gangue calcite indicates the mineralising fluids to be enriched in iron, manganese and lead, yet deficient in strontium.

CHAPTER SEVEN

The Detailed Geochemical Study of the Carbonates of the Wirksworth Area and a Discussion of the Possible Origins of the Dolostones

A quite detailed study of the geochemistries of the Hoptonwood and Matlock limestones and dolostones was undertaken to try and identify the origin of the dolomitising fluids. This involved the analysis of both major and trace elements of 180 limestone and dolostone samples from the study area. Many of the majors (Ca, Mg, Fe, Mn, Si and Al) and traces (Zr, Y, Zn, Ni, Sr and Pb) were analysed using the Energy Dispersive X-r-f (E.D.X.) method. The procedure is outlined in Appendix VI. The detection limits for sodium and potassium using this equipment are well above the mean values found in these rocks, therefore both sodium and potassium were analysed by Atomic Absorption Spectrometry using the standard method (Appendix V). The rare earth analyses were performed by Instrumental Neutron Activation Analyses following the procedure of Appendix VII.

A comparison of the limestone and dolostone chemistries shows quite significant differences and gives some indication of the origin of the dolomitising fluids. Comparable limestone and dolostone specimens were sampled by making numerous traverses across the dolostone boundary (fig. 13) although many dolostone samples from the Ryder Point and New Harborough Farm boreholes, within the Hoptonwood "Group", were also analysed.

7.1 Majors

7.1.1. Sodium

The detection limits of the E.D.X-r-f system are far above those required to analyse both sodium and potassium in the carbonates of this study, thus the analyses of these elements was performed using Atomic Absorption Spectrometry (Appendix V). The whole rock values plus the individual calcite and dolomite values, obtained by dissolution with acetic and nitric acid, are given in Appendix V. No significant leaching of sodium or potassium from the associated clay minerals during dissolution is evident, as shown by the plots of sodium or potassium concentrations in the calcite and dolomite against insoluble residue, as no increase of sodium or potassium occurs with increasing insoluble content (figs. 42A and 42B).

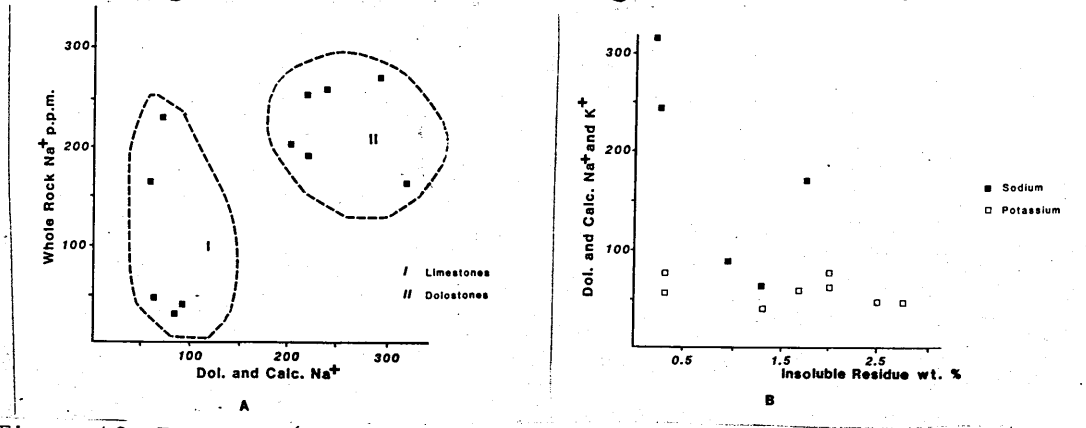


Figure 42 Plots of (A) the sodium contents of the soluble calcite and dolomite against the sodium contents of the whole rock limestones and dolostones, and (B) the sodium and potassium contents of soluble calcite and dolomite against the insoluble residues of the corresponding limestones and dolostones.

Only six limestone samples from scattered locations throughout the succession were used. Although the small number of samples places limitations upon the use of the information, the consistency of results particularly of the soluble calcite allows meaningful conclusions to be drawn from the values.

Table VIII shows the results obtained during this study and compares these with published data.

		Na^+ p.p.m.		
		Range	$\bar{x}$*	s*
Carboniferous Limestone, Wirkworth.	Whole Rk.	30-231	103.8	±91.1
	Calcite	65-88	75.0	±9.6
Ordovician Limestone (White 1977)			154.0	
Modern Carbonates (Land et al., 1975)		600-4000		
Open Marine Carbonates (Badiozamani 1973)		100-300		

* $\bar{x}$=mean s=standard deviation of the mean

Table VIII The sodium contents of the Wirksworth limestones, together with results, for similar rocks, found in the literature

The whole-rock sodium values shown in Table VIII can be seen to be highly variable and do not correlate well with the amount of insoluble residue present (fig. 42A). Considering the consistency of the sodium values of the calcite, the variability of the whole-rock sodium values seems to reflect the type of clay present, rather than the amount. For example, those samples which have correspondingly high sodium and insoluble residue content indicate the presence of a sodium-rich clay such as montmorillonite whereas low sodium values with high insoluble residue values reflect the presence of possible potassium-rich clays or quartz, very common in these limestones (see Section 3.2.9). As stated, the lack of correlation between insoluble residue and the sodium values of the soluble calcite indicates that the sodium values are not caused by leaching of clays, but represent sodium within the calcite lattice (figs. 42A and 42B).

The sodium values of the soluble calcite are more constant (Table VIII) having quite a narrow range with a mean of 75 p.p.m.. Modern carbonates have been shown to have a wide range of sodium values; 600 - 4000 p.p.m. (Land

et al. 1975) and 100 - 300 p.p.m. (Badiozamani 1973). A recent study by White (1978) shows the lower figure of 100 - 300 p.p.m. is more representative of modern carbonates, as the enhanced values represent secretion of invertebrate organisms. Thus it seems that the sodium values of these limestones are somewhat lower than modern carbonates (100 - 300 p.p.m.). Most of the analysed limestones have a considerable amount of sparry calcite, representing deposition within fresh waters (Section 3.2.6). The relative abundance of this spar accounts for the much lower sodium values of the limestones.

A similar number of samples of dolostones were analysed and similar limitations must be heeded, although again, the consistency of the range of sodium values in the soluble dolomite suggests a reasonable representation. Table IX contains the results obtained during this study and shows a comparison with published data.

		Na^+ p.p.m.		
		Range	$\bar{x}$	s
Dolomitised Carboniferous Limestone, Wirkworth.	Whole Rk.		230.8	±45.9
	Dolomite	235-344	267.8	±37.3
Primary Dolostone (Weber 1964)			264.0	
Secondary Dolostone (Weber 1964)			209.0	
Primary Dolostone (Fritz and Katz 1972)		200-600		
Secondary Dolostone (Fritz and Katz 1972)		0-200		
Primary Dolostone (Randazzo and Hickey 1978)			916.0	
Primary Dolostone (Veizer et al.,1978)		200-600		

Table IX The sodium contents of the Wirksworth dolostones, together with results, found in the literature, for similar rocks

In contrast to the limestone samples, the dolostone whole-rock sodium values are less variable and this may reflect the nature of the clays in the particular samples chosen, i.e. sodium-deficient residues. The soluble dolomite has

consistent sodium values varying little and have a mean of 267.8 $\pm$ 37.3 p.p.m.. The slight variation could reflect the presence of the varying amount of pore-filling calcite of freshwater origin (Section 3.2.6), although it is more likely to indicate the degree of inaccuracy in the method of analysis. It can be seen that the dolomite Na^+ values are far in excess of those values in the calcite. Prior to dolomitisation it is believed that the limestone had experienced several periods of exposure and thus had become stabilised under sub-aerial conditions, to low-magnesium calcite (Section 3.3). Thus, the sodium values are believed to be fairly representative of those in the limestones prior to dolomitisation. The higher values of the dolomite must either represent a greater partitioning of sodium into dolomite under different conditions or more highly saline dolomitising fluids. White (1978) has suggested experimentally that there is probably little difference in the partition coefficients for either calcite or dolomite and that these do not vary greatly with pH. It seems probable then that the higher sodium values represent the presence of more saline water during dolomitisation. Weber (1964), Fritz and Katz (1972), Land and Hoops (1973) and Veizer et al. (1977/8) have all studied the sodium contents of primary and secondary dolostones, giving a range of 0 - 200 for secondary dolostones and 200 - 600 reflecting a more hypersaline environment. Calcium carbonate precipitated in modern oceans has been shown to have sodium values of around 200 p.p.m., and following the work of White (1978), dolomites developing in similar environments should have similar values. It seems likely, therefore, that the value of 230 p.p.m. Na^+ which Veizer et al. (1977) used

to distinguish between open marine and hypersaline waters is reasonably correct. This agrees quite well with the values of 200 - 700 p.p.m. and 916 p.p.m. for hypersaline brines given by Fritz (1971) and Randazzo and Hickey (1978), respectively. Land et al. (1975) have shown recent dolomites to have sodium values ranging between 600 and 4000 p.p.m., and the much lower values of other dolomites have been suggested by Badiozamani (1973) to represent their formation in brackish water, the lower sodium content being due to the presence of less saline groundwater. However, the values of 200 - 700 p.p.m. for supratidal dolomite given by Fritz (1971) were supported by isotopic data which also indicated hypersaline conditions. If the crystallisation of the dolomite had occurred in brackish water, then it is this which would be reflected in the isotopic data, rather than a former hypersaline environment. White (1978) suggests that the much higher values represent biogenic material and that the associated proteins and polypeptides may have enhanced the co-precipitation of Na^+. The results of White agree quite well with the values of Fritz (1971) and Veizer et al. (1977) and thus a reasonable distinction between open marine and hypersaline conditions may exist below and above 200 - 230 p.p.m. Na^+ respectively.

The sodium values for the dolostones of this study support a hypersaline nature for the dolomitising fluid. However, the values are not as high as many of the values given for hypersaline conditions by Fritz (1971) and Randazzo and Hickey (1978); instead the values seem to be

much closer to normal marine conditions. In fact sodium values in either calcite or dolomite will depend upon the mNa^{+}/mCa^{2+} of the solution rather than the salinity. Thus the values of these dolostones, rather than reflecting any particular salinity, represent the mNa^{+}/mCa^{2+} of the dolomitising solution.

7.1.2. Potassium

The difficulties encountered during the analysis of potassium have been outlined in Section 7.1.1 and consequently it was analysed by Atomic Absorption Spectrometry. As with sodium, both the analysis of whole-rock and constituent calcite and dolomite (by dissolution) was performed.

		Range	K^{+} p.p.m. $\bar{x}$	s
Carboniferous Limestone, Wirkworth.	Whole Rk.	48-503	201.3	±180
	Calcite	38-63	51.5	±9.9
Limestone (Clarke 1924)			2739.0	
Dolomitised Carboniferous Limestone Wirksworth.	Whole Rk.	91-410	166.2	±137.1
	Dolomite	57-144	91.0	±33.0
Primary Dolostone (Weber 1964)			227.0	
Secondary Dolostone (Weber 1964)			138.0	
Primary Dolostone (Fritz and Katz 1972)		600-2000		
Secondary Dolostone (Fritz and Katz 1972)			800.0	

Table X The potassium contents of the Wirksworth limestones and dolostones, together with results, found in the literature for similar rocks.

Again, no significant leaching of potassium from the clays during dissolution could be proven (fig. 43). The results of this study are given in Table X and compared to other published data.

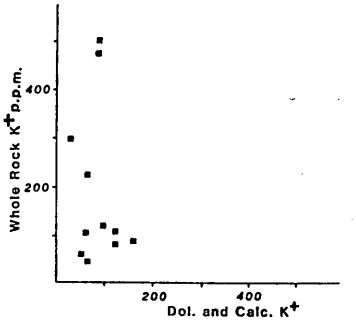


Figure 43 A plot of the potassium contents of soluble calcite and dolomite against the whole rock potassium contents of the limestones and dolostones

The whole-rock potassium contents of limestones and dolostones are shown to be very variable, which may be

expected due to the common occurrence of K^+ in many clay minerals, and thus variable whole-rock K^+ reflects the variation in the potassium values of the insoluble residues. The soluble calcite and dolomite show two distinct ranges of K^+ and are found to be independent of insoluble residue and thus are contained within the lattice of the calcite and dolomite. The limited study of the behaviour of K^+ in different salinities has shown it to be highly variable and unreliable, and less definitive than sodium. The soluble phases of the limestones and dolostones show two distinct ranges and again indicate an enriched dolomitising fluid. However, the values of the dolomite are well below those given by Weber (1964) for hypersaline conditions i.e. 227 p.p.m.. Correspondingly, lower sodium values also occur and although the values indicate solutions enriched in sodium and potassium relative to sea water, these do not indicate very hypersaline conditions. Additionally, Veizer et al. (1977) have shown that at higher salinities the coprecipitation of K^+ is inhibited and this may account for the much lower potassium value found in these dolostones. It is clear that further work is required before potassium can be used as a reliable salinity indicator.

The analysis of the other majors (Mg, Ca, Fe, Mn, Si and Al) and traces (Zr, Y, Zn, Ni, Sr and Pb) was much more extensive, involving 180 samples, and carried out using the E.D.X..

7.1.3. Magnesium

The magnesium content of any limestone will be highly variable and unpredictable, due to variability of the

original mineralogy and later diagenesis (Chapter III). Table XI gives the values found in these limestones and shows that there are two distinct ranges and that they are dependent upon facies.

		$MgCO_3$%		
		Range	$\bar{x}$	s
Carboniferous Limestone, Wirkworth.	Micarenites	0.14–0.33	0.26	±0.09
	Sparenites	0.06–0.23	0.13	±0.06

Table XI The $MgCO_3$ contents of the Wirksworth limestones.

Originally, the lime muds and sands essentially consisted of aragonite and high-magnesium calcite. The aragonite contributes little to the overall magnesium value due to its low magnesium content. High-magnesium calcite (12 - 17% $MgCO_3$) occurs as both allochems (the percentage of $MgCO_3$ is dependent upon variables such as temperature, Chave 1954, Moberly 1970) in limes muds and later as a primary cement around many of the interparticle pores. The instability of high-magnesium calcite under sub-aerial conditions results in its recrystallisation to low-magnesium calcite. Evidence for the former high-magnesium calcite is seen in the higher magnesium values (1.5%) remaining in the low-magnesium calcite, which is not evident after the replacement of aragonite (Davies 1977). In the more sparry limestone, later diagenesis has introduced a low-magnesium cavity-fill cement (Table IV) and this has produced the lower magnesium values. Table IV shows that the other major constituents of these limestones (viz micrite)is relatively enriched in magnesium. As discussed in Chapter III, micrite may have a number of origins and consequently a number of mineralogies. The relatively low Mg value of the micritic material, although greater than the sparry material, does not suggest a great amount

of high-magnesium calcite present in the former lime mud, although it must be appreciated that total loss of magnesium may have occurred during diagenesis. However, the higher strontium values (Section 7.2.1) support an aragonitic precursor.

The mineralogy of the allochems may further complicate the matter as many fossils contain high magnesium percentages. The most common allochems of these limestones are the crinoidal fragments, which represent formerly high-magnesium calcite. Here, the high-magnesium calcite precursor is reflected in the relatively high magnesium values of crinoidal-rich limestones (sample $L_1$6m).

7.1.4. Calcium

The CaO/MgO ratios (wt.%) of the whole-rock dolostone analyses vary quite considerably and reflect the amounts of free calcite either as pore-filling cements or dedolomitisation. Ideal dolostone, that is to say dolostone with no excess calcite, would have a CaO/MgO ratio of 1.39. Table XII indicates the variation of the CaO/MgO that occurs in the dolostone.

	CaO/MgO		
	Range	$\bar{x}$	s.
Dolomitised Carboniferous Limestone, Derbyshire.	1.38-2.16	1.47	± 0.32

Table XII. The CaO/MgO ratios of the Wirksworth dolostones.

Microprobe analysis has allowed the study of the stoichiometry of individual dolomite crystals. The results (Table VI) consistently indicate good stoichiometry i.e. 50 mol% $CaCO_3$. Slight variations of this stoichiometry occur and are shown

to be calcium-rich. As stated, the dolomite is stoichiometric, therefore the calcium-rich nature is believed to be either a consequence of small calcite remnants in the dolomite, similar to those described by Evamy (1967) or intracrystalline dedolomitisation (Section 4.4.5) and does not represent a non-ideal dolomite (Goldsmith and Graf 1958). Folk and Land (1975) and Weaver (1975) have suggested that a more ideal dolomite may develop as a result of slower crystallisation in less saline waters, in contrast to the non-ideal nature of dolomite so commonly associated with hypersaline conditions, induced by rapid crystallisation (Alderman and Skinner, 1957, Deffreyes et al., 1965, Shinn et al., 1965). However, Goldsmith and Graf (1958), Illing et al. (1965) and Marschner (1968) show that ideal dolomite can occur associated with hypersaline conditions, which would correspond more closely to that indicated by the sodium values.

7.1.5. Iron

The Fe_2O_3 values vary quite considerably from limestones to dolostones, giving two distinct means, 0.05% and 0.47% respectively. Table XIII indicates the ranges of Fe_2O_3 for the dolostones and limestones and are compared with published data.

The limestones show a large range of values, varying from 0.02 - 0.16 percent. Table XVIII indicates that, as with the strontium values (Section 7.2.1), the ferroan content

of the limestones appears to fall in the sparentites, due to the presence of non-ferroan cements. These sparenites (with abundant cement) give very low Fe_2O_3 values (0.02 - 0.03%) and indicate very low real values. Microprobe analysis (Table VI) has confirmed the low ferroan nature of these cements, and together with X-r-f analyses show the micritic members to have much higher Fe_2O_3 values than the sparenites, as well as being more variable (0.04 - 0.11%). Richter and Fuchtbauer (1978) have given a value of 1.00 for the partition coefficient of iron in calcite at 25°C and pH's around 7. Under normal marine conditions although the noted iron content of sea water is variable, a value of 20 - 70 p.p.m. would be expected in calcite. Therefore, the value of the micritic calcite is much higher than that expected.

The relatively higher concentration of iron in the micritic lithologies may have the following explanations: (1) as Fe_2O_3 occurring as a coating deposited by goundwater (2) associated with the clay minerals or (3) iron sulphides. The Matlock "Group" does appear much darker in hand specimen, but this is due to the presence of hydrocarbons (Section 2.3), rather than to iron, additionally the Hoptonwood "Group" does not show any coloration, even though much of its more micritic units have similarly high Fe_2O_3 values (0.09% Fe_2O_3, sample HW26).

Figure 44A shows that a quite good correlation exists between the insoluble residue and the Fe_2O_3 content. The

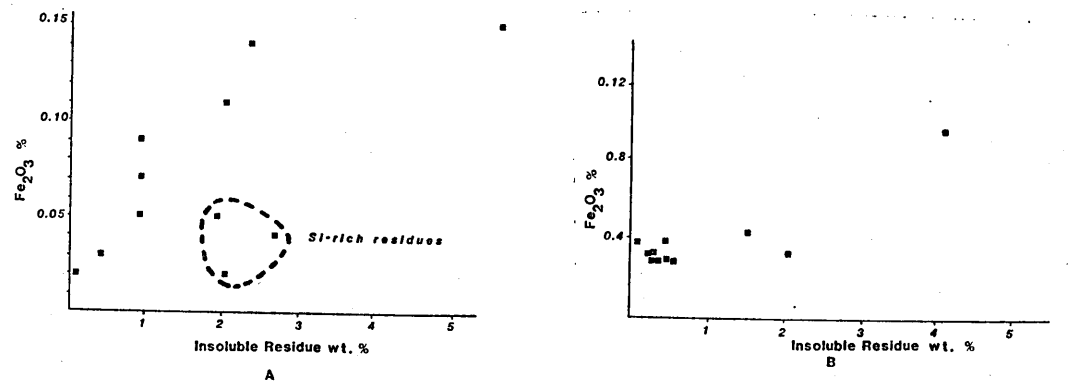


Figure 44 Plots of Fe_2O_3 % against insoluble residues of (A) the Limestones and (B) the dolostones

presence of the Si-rich residues indicates that the type of residue is very important. If the origin of this correlation is the clay minerals, then it seems likely that a more positive correlation would be evident in the dolostones (fig. 44B). However, the lack of any correlation between dolostones and insoluble residues suggests that some other source of iron is present in the limestones which does not occur in the dolostones. The limestones of the Wirksworth area can be seen to be associated quite commonly with goethite (after pyrite). The quiet water conditions under which the more micritic members of the succession were deposited, would be ideally suited for the production of anaerobic conditions. These quiet conditions would allow bacteria to form sufficient sulphide to combine with available Fe^{2+} (under reducing conditions) to give pyrite, thus accounting for the variable and high iron content of the micrites and the fairly good correlation with the insoluble residue. Two distinct ranges of Fe_2O_3 values between the micarenites and sparenites account for the high correlation coefficient

(0.99) between iron and aluminium (Appendix VI). The lack of iron oxide in the sparenites reflects the abundance of non-ferroan calcite and sandy, well-oxygenated nature of its original deposition, due to the constant flushing of seawater. The constant regeneration of the oxygen content of the pore waters does not allow the development of reducing conditions and the formation of pyrite. A regression line drawn through the points of figure 44A may indicate an original Fe_2O_3 value of approximately 0.012-0.015% for the constituent calcite. This value is much closer to that predicted for calcite precipitated from seawater.

	$FeCO_3$ %		
	Range	$\bar{x}$	s
Carboniferous Limestone, Wirkworth	0.02-0.16	0.058	±0.036
Average Limestone (Clarke 1924)		0.54	
Dol. Carboniferous Lst, Wirkworth	0.16-2.86	0.47	±0.42
Primary Dolostone (Weber 1964)		0.39	
Secondary Dolostone (Weber 1964)		0.39	

Table XIII The Fe_2O_3 contents of the Wirksworth limestones and dolostones, together with results, found in the literature, for similar rocks.

The dolostones show a similar variability of iron oxide as seen in the limestones (Table XIII). However, a similar correlation between iron and insoluble residues (fig. 44B) does not occur and thus the iron material seems to be associated with the lattice. The much higher Fe_2O_3 values found in some dolostones can be related to higher iron concentrations associated with extensive dedolomitisation, examples of this can be seen in the borehole and traverse samples (Section 5.3.5). Under the oxidising conditions of the dedolomitisation process, the iron fails to be incorporated within the calcite lattice and forms a coating of either iron oxide or hydroxide (Section 4.4.5). Where the

dedolomitisation is extensive, it can contribute quite significantly to the dolostone iron oxide values. This accounts for the high iron concentration associated with some dolostones shown in figure 44B.

If we study the remainder of the dolostones, then a mean value of $0.375 \pm 0.144\%$ for the Fe_2O_3 contents is obtained. This corresponds very well with the 0.35 percent value given by Weber (1964) for primary dolostones, formed under hypersaline conditions (which the sodium values of these dolostones may indicate). From the uniformity of the iron oxide values, the lack of correlation between Fe_2O_3 and insoluble residue and microprobe data given in Table VI, the the iron is believed to be accommodated within the dolomite lattice, mainly substituting for Mg^{2+} (Wyckoff and Merwin 1924). The much higher values of the Derbyshire dolostones compared with the limestones are a consequence of a greater partition coefficient of iron in magnesium-rich carbonates such as dolomites and a rise in the Fe^{2+} content of the dolomitising brines. No data are available for the partition coefficient, yet a greater partitioning is assumed due to the affinity iron has for magnesium. The Fe_2O_3 rise cannot be accounted for solely by its partition coefficient, as to give an iron oxide percent of 0.375, a partition coefficient of 1285 would be required which is highly unlikely, As well as an increased partition coefficient, a rise in the iron content of the

solution also seems likely if the conditions of deposition eg. pH, are not markedly different. These much higher iron contents can be characteristically formed in water of low Eh, possibly due to stagnation, and the introduction of reducing conditions. These reducing conditions allow a rise in the more soluble ferrous ions.

Iron can be concentrated in many environments such as groundwater (Champ et al., 1979) and hypersaline brines. The rise in Fe_2O_3 of hypersaline solutions is indicated by the quite high values of primary dolostone (Weber 1964) and the analyses of calcite and dolomite from the Coorong in S.E. Australia by Alderman and Skinner (1957). Hypersaline brines represent either environments where no regeneration of the oxygen levels occurs from constantly inflowing fresh seawater, such as in restricted lagoons and sabkhas or fluid of greater density making it difficult for mixing with well oxygenated sea water to occur. Under the stagnant conditions and in the presence of bacteria the oxygen levels fall and induce reducing conditions and thus allow the soluble iron to rise in the solution.

7.1.6. Manganese

Table XIV shows the mean values of manganese obtained from the limestones and dolostones of the Wirksworth area and a comparison of these data with other published results

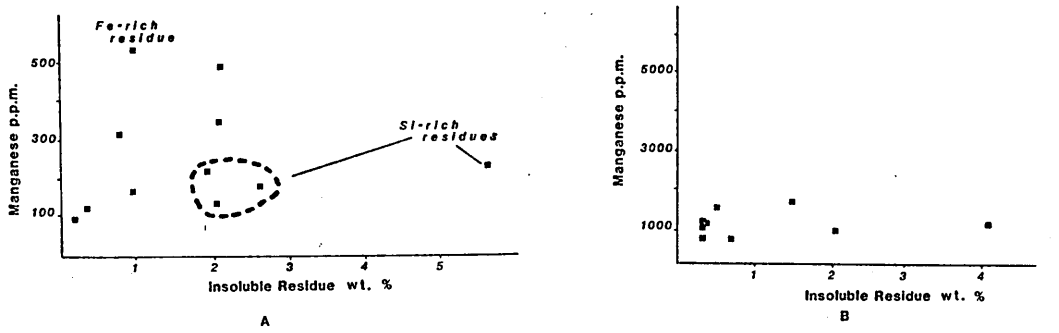


Figure 45 Plots of manganese contents against the insoluble residues of (A) the limestones and (B) the dolostones.

Like iron oxide, the manganese values of the limestones are also variable. In view of the lack of correlation with the dolostone and insoluble residues (fig. 45B), it is believed that the manganese is not associated with the clay minerals. Table XVIII indicates that the manganese content tends to be greater in the more micritic limestones, although this is

	Mn^{++} p.p.m.		
	Range	$\bar{x}$	s
Carboniferous Limestone, Wirksworth	93.8-1409	344.0	±311.0
Carb.Lst.N'land (Al-Hashimi 1973)		336.0	
Average Dev. and Carb Lst.(Veevers 1969)		346.0	
Dol.Carboniferous Lst,Wirksworth.	602.5-5645	1200.0	±816.0
Primary Dolostone (Weber 1964)		245.0	
Secondary Dolostone (Weber 1964)		237.0	
Carb.Lst.N'land (Al-Hashimi 1973)		2070.0	

Table XIV The manganese contents of the Wirksworth limestones and dolostones, together with results, found in the literature for similar rocks

not as marked as the increase in iron oxide content. Manganese tends to have a great affinity for iron and so the most likely explanation of this rise in the micrites is the presence of pyrite. Certainly the values in these calcites cannot be a consequence of simple precipitation of calcite from seawater, as this would give a much lower Mn^{2+} value in the region of 2×10^{-3} p.p.m. considering a partition coefficient of 15 (Pingitore 1978).

The manganese values of the dolostones show a similar variation to the Fe_2O_3 values. This is due to its association with iron ($r = 0.08$, Appendix VI)

in the dolomitised samples mentioned in Section 5.1.5. Even allowing for these much higher values the manganese content of the remainder of the dolostones is still higher (1140 p.p.m.) than the limestones. The lack of correlation between manganese content and insoluble residue (figure 45B) indicates that the manganese is included within the dolomite lattice. The higher values are greater than those given by Weber (1964) for primary dolostones, but well below the values given by Al-Hashimi (1971) for Northumberland dolostones believed to be derived from groundwater. Again the rise in the manganese in dolomites can be attributed to a higher partition coefficient and a rise in the manganese content of the dolomitising fluids. As indicated in Section 7.1.5, the partition coefficient cannot be solely responsible for this manganese increase as this would require a ridiculously high figure, even though the partition coefficient is expected to be greater than that of calcite due to the tendency of manganese to substitute for magnesium in the dolomite lattice (Wyckoff and Merwin 1924). The rise in the manganese content of the original dolomitising fluids can be attributed to the similar reducing conditions which produced the much higher iron concentrations.

7.1.7. Silica

Table XV indicates the great variation of silica contents that occurs in the carbonates. Both the limestones and dolostones are comparatively free of clay and show a great deal of silica variation.

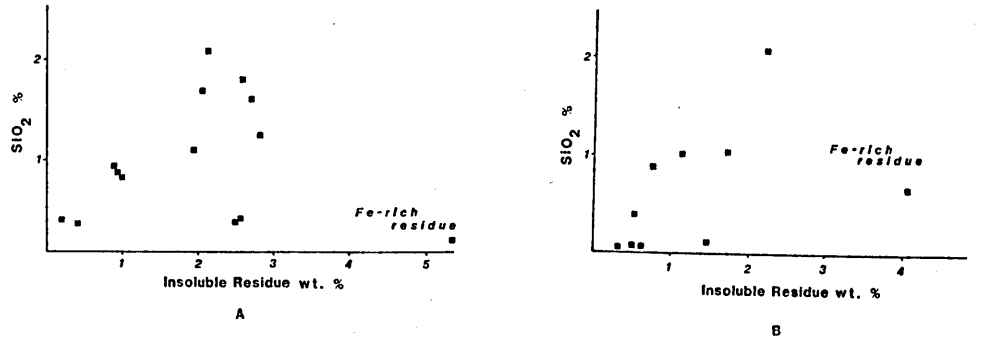


Figure 46 Plots of SiO_2 % against the insoluble residues in (A) the limestones and (B) the dolostones.

The correlation between silica content and insoluble residues is weak due to the presence of high iron residues, probably occurring as pyrites (Section 7.1.5) (figs. 46A and 46B).

	SiO_2 % Range
Carboniferous Limestone, Wirksworth	0.03-2.10
Dol. Carboniferous Lst., Wirksworth	0.00-0.47

Table XV The SiO_2 contents of the Wirksworth limestones and dolostones.

Section 7.1.5 (fig. 44A) shows that in particular these high insoluble residues indicate iron-rich samples and probably represent an abundance of pyrite in the limestones and ferric compounds associated with dedolomitisation in the dolostones.

7.1.8. Aluminium

The aluminium content of the Wirksworth carbonates has been found to be very variable (Table XVI). Normally one would expect the aluminium to be associated with the clays in limestones and dolostones, however, the correlation coefficients for Al and Si (Appendix VI) are poor

	Al_2O_3 % Range
Carboniferous Limestone, Wirksworth	0.00-1.76
Dol. Carboniferous Lst., Wirksworth	0.00-0.47

Table XVI The Al_2O_3 contents of the Wirksworth limestones and dolostones.

An explanation for this poor correlation, already given in Section 7.1.7, is that it is caused by the presence of iron-rich phases such as pyrite as well as free silica, occurring as quartz crystals. This gives high insoluble residue contents but low Al_2O_3 values. If we correct for these effects then it can be seen from figure 47 that a good correlation exists between the insoluble residue and Al_2O_3.

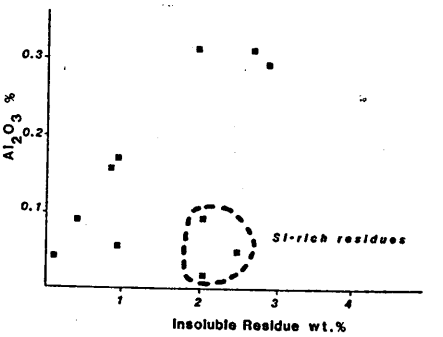


Figure 47 A plot of Al_2O_3 % against the insoluble residues in the limestones.

Table XVIII again shows an association of Al_2O_3 content with the more micritic limestones which reflects the similarity in depositional environments of fine grained carbonate and aluminosilicate material. The sparenites tend to have a much lower Al_2O_3 content because of the absence of the much finer grained aluminosilicate.

The Al_2O_3 content of the dolostones tends to be much lower, indeed it is often below the detection limits of the analysis (Appendix VI). This is thought to be caused either by a loss of clay minerals during dolomitisation, indeed the dolostones show a decrease of insoluble residues or a loss of Al from the clay due to leaching by the dolomitising brines. A similar loss of aluminium during dolomitisation was noted by Al-Hashimi (1971)

in Northumberland dolostones.

7.2. Trace Elements

The analysis of trace elements (except for the Rare Earth Elements), was performed using pelleted samples for use with the Energy Dispersive X-r-f. The procedure used and the detection limits of the method are outlined in Appendix VI. The Rare Earth Elements were analysed by Instrumental Neutron Activation Analysis (Appendix VI).

7.2.1. Strontium

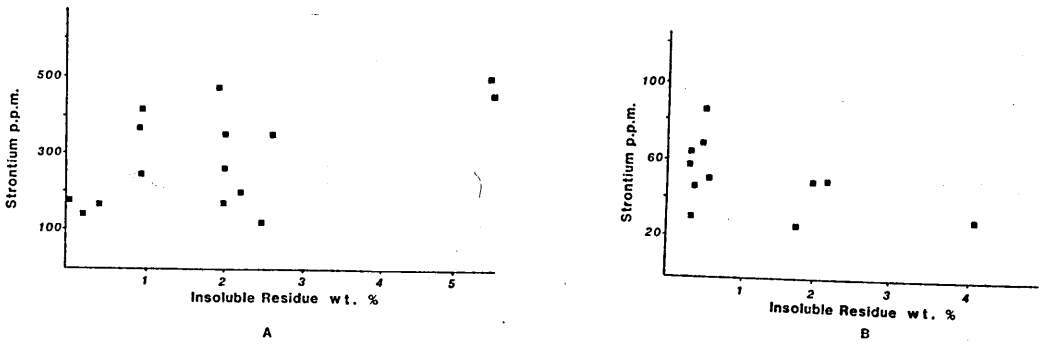


Figure 48 Plots of strontium contents against the insoluble residues in (A) the limestones and (B) the dolostones.

Table XVII indicates that strontium is clearly more concentrated in the micarenites (335.8 - 484.5 p.p.m.) than in sparenites (140.1 - 207.7 p.p.m.) which was also noted with iron, manganese and aluminium. This is due to the micritic material being a product of the recrystallisation

of strontium-rich aragonite or high-magnesium calcite. The sparenites tend to be lower because of the presence of low strontium meteoric sparry calcite. The association of these high strontium levels with the micritic material accounts for the fair correlation of strontium with the insoluble residues (figure 48). It is thought that the strontium is included within the lattice rather than within clay minerals etc; as no positive correlation occurs between strontium and either aluminium or silica. The fair correlation with the insoluble residue (figure 48A) and iron (Appendix VI) is a consequence of clay minerals and pyrites, also being associated with micritic material.

	Sr^{++} p.p.m.		
	Range	$\bar{x}$	s
Carboniferous Limestone, Wirksworth.	72.5-484.5	218.5	±132.0
Carb.Lst.N'land (Al-Hashimi 1973)		132.0	
Average Limestones (Bausch 1965)		610.0	
Dol.Carboniferous Lst., Wirksworth	24.2-98.6	59.7	±16.8
Carb.Lst.N'land (Al-Hashimi 1973)		618.0	
Primary Dolostone (Weber 1964)		174.0	
Secondary Dolostone (Weber 1964)		187.0	
Dedolomitic Lst.N'land (Al-Hashimi 1973)		187.0	
Dedol.Lst.Juras (Shearman and Shirohammadi 1966)		95.0	

Table XVII The strontium contents of the Wirksworth limestones and dolostones, together with results, found in the literature for similar rocks.

Strontium has become a major tool in unravelling the complex diagenesis of carbonate minerals although conflicting partition coefficients for strontium into calcite exist. Kinsman (1969) proposed a partition coefficient of 0.14 at 25°C and this was independently confirmed by Oxburgh et al. (1959) and both of these are higher than that of Katz et al. (1972), which is 0.055 at 40°C.

The micritic material is thought to have been an aragonitic lime mud, due to absence of any significant

amounts of magnesium (Section 7.1.3.). Later it underwent subaerial diagenesis causing the formation of micrite and microsparite(formed by neomorphic aggradation). Originally, this aragonite lime mud may have contained between 7000 and 10,000 p.p.m Sr^{2+}, if we can draw on analogy with Kinsman's (1969) studies of modern carbonates. Diagenesis of the aragonite to low-magnesium calcite under subaerial conditions, considering the partition coefficient of Kinsman, would allow a calcite to develop with a Sr^{2+} concentration of approximately 1,000 p.p.m. This assumes that the mSr^{2+}/mCa^{2+} of the dissolved aragonite, which the strontium partitioning is dependent upon, dominated the chemistry of the precipitating fluids. The much lower ranged values of the micrites of this study (viz. 335.8 - 484.5 p.p.m) may indicate that a significant portion of the dissolving and precipitating fluids was meteoric which is characterised by a low strontium content. Certainly Folk (1965) believes a fluid phase to be involved during aggradation of crystals (Section 3.2.4.) and Longman (1980) believes that fluids may adequately be supplied in the active freshwater phreatic zone. Another explanation for the lower strontium values could be the excessive amounts of formerly high-magnesium calcite, lower strontium fossils, such as crinoids, occurring in the micarenites. The original high-magnesium calcite would have a Sr^{2+} content of approximately 1200 p.p.m. which upon diagenesis in a closed system and using Kinsman's value, would give similar values to those found in these micrites ie. 300 - 400. Thus if significant amounts of

(A) MICRITE DOMINATED LIMESTONES

SAMPLE Nos.	FeO	MnO	Al_2O_3	Sr^{2+}	MgO	CARBONATE TYPE and Brief Description.
HW4	0.09	533.7	0.16	369.0	0.27	Br. Biomicarenite
IQ3	0.04	170.1	0.31	403.7	0.26	Br. Biomicrosparenite
$L_2$7	0.14	241.3	1.76	444.1	0.41	Br. Biomicrosparenite
$L_2$5	0.11	354.6	0.09	335.8	0.14	Br.-Al. Biomicarenite
$L_6$3	0.05	154.6	0.44	484.5	0.33	Biomicarenite
1A	----	-----	----	359.2	----	Biomicarenite
2A	0.05	496.3	0.08	388.5	0.30	Br. Biomicrosparenite
5A	----	-----	----	368.9	----	Br.-Gr. Biomicarenite
IQ2C	0.05	164.2	0.17	413.9	0.29	Foss. Pelsparenite-many peloids
$L_2$10	0.04	239.0	0.02	328.1	0.24	Cosparenite
$L_6$6	0.05	207.3	0.32	478.4	0.13	Cr.-Br. Pelsparenite-many peloids

(B) SPAR DOMINATED LIMESTONES

SAMPLE Nos.	FeO	MnO	Al_2O_3	Sr^{2+}	MgO	CARBONATE TYPE and Brief Description
HW1	0.02	93.8	0.04	140.1	0.01	Cr.-Al. Biosparenite
HW8	0.03	123.9	0.09	160.3	0.11	Cr.-Al. Biosparenite
3B	0.02	156.1	0.10	197.9	0.14	Biosparenite
4B	0.02	122.6	0.09	170.4	0.23	Biosparenite
6C	----	-----	----	195.6	----	Cr. Biosparenite
8A	0.07	184.4	0.29	207.7	0.13	Cr. Pelsparenite
8B	0.07	670.0	0.02	124.8	0.06	Foss. Pelsparenite-many crinoids
IQ7	0.07	558.0	0.06	242.9	0.16	Cr.-Al. Pelsparenite
$L_4$6	0.02	130.1	0.02	251.9	0.59	Cr. Biomicarenite-many crinoids
3A	0.03	129.0	0.08	246.0	0.16	Cr. Biomicarenite-some peloids
7A	0.09	185.8	0.06	105.8	0.13	Cr. Biomicarenite-many crinoids with good syntaxial rims

Table XVIII A comparison of the chemistries of the different limestone types.

biogenic calcite occur in the micrites, then a marked decrease in the strontium level would occur. This accounts for the anomalous lower values of crinoidal-rich biomicarenites compared to other micarenites (Table XVIII). The original high Sr^{2+} content of 1,450 p.p.m (Graf 1960) of these crinoidal fragments upon stabilisation gives a value of 203p.p.m (Kinsman)or 80 p.p.m (Katz et al.) in a closed system which is unlikely, as discussed above and thus subaerial weathering probably introduced strontium-deficient solutions thus reducing the Sr^{2+} values further, accounting for the lower values of these crinoidal-rich micarenites.

Consider now the much lower partition coefficient i.e. 0.055 of Katz et al., (1972), under similar conditions to above. Subaerial diagenesis of an aragonitic sediment in a closed system would give a 400 - 600 p.p.m Sr^{2+} content in the low magnesium calcite. These are more in accord with the values given in the limestones although their slightly lower values may again indicate the presence of strontium - deficient meteoric water during dissolution - reprecipitation, or the presence of former high-magnesium calcite. Therefore whichever partition coefficient is considered it would appear that meteoric water may have had a significant role in the stabilisation of the lime muds.

The much lower Sr^{2+} values of the sparenites are a consequence of the presence of strontium poor, sparry cements of freshwater origin. Kinsman (1969) gives a mSr^{2+}/mCa^{2+}

value for groundwater of 0.32 and the precipitation of spar from these solutions in interparticle pores would significantly reduce the whole rock Sr^{2+} values.

Exceptions to these two categories given in Table XVIII are the relatively strontium-rich pel- and oosparenites and relatively strontium-poor, crinoidal rich pelsparenites and micarenites. The higher values of the pel- and oosparenites are a consequence of the aragonitic nature of the former peloids and ooids, and thus although the Sr^{2+} values are lowered by the presence of secondary spar, they still retain quite high concentrations of strontium. The lower values of the crinoid-rich pelsparenites and micarenites have been discussed above and are caused by the former high-magnesium calcite of the crinoids.

The range of Sr^{2+} values in the dolostone is less variable and relatively lower than in the limestones. The values are similar to those given for primary dolostones (Table XVII) but lower than similar secondary dolostones in Northumberland which Al-Hashimi (1971) gave as 618 p.p.m but are similar to values (80 - 99 p.p.m) found in dolostones formed due to mixing of freshwater and seawater, given by Land et al., (1975).

Some idea of the composition of the dolomitising fluids can be derived by studying the partition coefficient of strontium in dolomite (K_{Sr}^{Dol}), if we assume no recrystallisation of the dolomite has occurred. No accurate

determination of the K_{Sr}^{Dol} has been made, due to the difficulty of synthesising the mineral, however, estimates of 50 percent of that given for calcite have been suggested by Al-Hashimi (1976) and Jacobean and Udowski (1976). If we consider the dolomite crystals to have 59.7 p.p.m. Sr^{2+} (see Table XVII), then the initial mSr^{2+}/mCa^{2+} of the dolomitising fluids would be either 0.09×10^{-2} (using $K_{Sr}^{Dol} = 0.07$ after Kinsman 1969) or 0.24×10^{-2} (using $K_{Sr}^{Dol} = 0.0275$ after Katz et al. 1972) at approximately surface temperatures, and pH of approximately that of sea water. Dolomitisation may have occurred at depth and close to 100°C, i.e. at approximately 3,000 metres. At this temperature the partition coefficients are lower and much closer and give mSr^{2+}/mCa^{2+} for the dolomitising fluids of 0.17×10^{-2} ($K_{Sr}^{Dol} = 0.038$, Kinsman 1969) and 0.22×10^{-2} ($K_{Sr}^{Dol} = 0.029$, Katz et al. 1972), assuming similar pH's to those occurring in seawater, the latter have been proven from boreholes. These values are far below the mSr^{2+}/mCa^{2+} for seawater which is 0.88×10^{-2} and hypersaline brines which is $0.8 - 1.5 \times 10^{-2}$ according to Kinsman (1969). Dolomitisation by seawater would endow the dolomites with Sr^{2+} values of 550 p.p.m. (0.07×10^{-2} at 25°C) and 210 p.p.m. (0.0275×10^{-2}) and at 100°C, 300 p.p.m. (0.038×10^{-2}) and 225 p.p.m. (0.029×10^{-2}). The calculated values of the mSr^{2+}/mCa^{2+} of the dolomitising brines are closer to, yet still lower than, groundwater. Badiozamani (1973), however, states that the strontium content of calcite will depend not only upon the mSr^{2+}/mCa^{2+} but also on the $mCa^{2+}_{Solid}/mCa^{2+}_{Liquid}$. Thus, as the concentration of the solution increases then

the strontium value will fall. For example, doubling the calcium content of the dolomitising solution would cause a 50 percent drop in the strontium value. This allows another means by which these low strontium values may be explained. The significance of this factor upon the origin of the dolomitising fluids is discussed in the hypotheses of the origin of the dolomitising brines in Section 7.3.

A further source for the strontium exists in the parent limestone ie. in a virtually closed system where the chemistry of the dissolving calcite was able to dominate the dolomitising brines. The limestones probably had similar Sr^{2+} values to those given by the recent analyses of the limestone, as extensive diagenesis had occurred prior to dolomitisation (Section 3.3.). If the strontium of the dolomite was inherited from the former limestones then values of 11 - 28 p.p.m. from micrites and 4- 10 from sparenites (the variation is due to the variability of the K_{Sr}^{Dol}) would be expected which are far below those recorded in the dolostones. It is possible that the limestones had a higher strontium content than that found today prior to dolomitisation which would explain the much higher contents of the dolomites. There are a number of objections to this hypothesis; including (i) this would require a molecule for molecule replacement rather than a volume for volume, which is advocated herein (see Chapter IV) (ii) that a similar wide variation of strontium values should occur

in the dolostones, mimicing the differences between former micarenites and sparenites, but no evidence for this has been noted in the many dolostones studied and (iii) the sodium, iron and manganese values indicate a geochemical dominance of the dolomitising fluids in the environment of deposition of the dolostone.

Further diagenesis in the form of dedolomitisation (Section 4.4.5) has been shown by Shearman and Shirmohammadi (1969) and Al-Hashimi (1971) to produce lower strontium values (Table XVII). The dolostones that are significantly affected by dedolomitisation in this study show no significant loss of strontium.

7.2.2. Zinc

The zinc contents of these carbonates can be seen

	Zn^{++} p.p.m.		
	Range	$\bar{x}$	s
Carboniferous Limestone, Wirksworth	0.0-88.1	32.0	±35.0
Dol. Carboniferous Lst., Wirksworth	15.1-158.6	52.2	±33.8

Table XIX The zinc contents of the Wirksworth limestones and dolostones.

to be highly variable (Table XIX). This variation is thought to be primarily caused by the presence of mineralisation. Very little work has been done on zinc, in either limestone or dolostone. The most useful paper on this trace element is that of Pingitore (1978) who discusses the partitioning of zinc within marine and meteoric carbonate using a K_{Zn}^{Calc} value of 5.2.

Pingitore gave a zinc value of 19.1 p.p.m. for biogenic aragonite, but no value for inorganic carbonate. The partition coefficient of 5.2 would give a Zn value of 3×10^{-3} p.p.m. for calcite inorganically precipitated from seawater. The quite good correlation coefficient with silica and lack of correlation with strontium (Appendix VI), suggests that Zn is present in the insoluble residue. The much higher values are probably due to the influence of the lead-zinc mineralisation.

The zinc content in the dolostone is variable and the mean value is quite low. Dolostones unaffected by mineralisation and which have little insoluble residue have very low zinc values, in fact they are similar to those of calcite. One might expect much higher Zn values than in limestones in view of the tendency for zinc to substitute for Mg in the dolomite lattice. However, if we consider the dolomitising fluids to have a partition coefficient which is ten times that of calcite and a zinc concentration that is a hundred times that of seawater, the resulting concentration would be far below the detection limits of our equipment. Therefore, the much higher values must represent either a considerable enrichment of Zn in the dolomitising fluid or the influence of lead-zinc mineralisation The latter seems more likely.

7.2.3. Lead

	Pb^{++} p.p.m.		
	Range	$\bar{x}$	s
Carboniferous Limestone, Wirksworth	5.5-86.5	27.7	±29.0
Dol. Carboniferous Lst, Wirksworth	10.0-180.5	21.5	±17.0
Primary Dolostone (Weber 1964)		68.2	
Secondary Dolostone (Weber 1964)		18.2	

Table XX The lead contents of the Wirksworth limestones and dolostones.

As with the zinc values (Table 20) the lead content of these limestones and dolostones is very high and variable and reflect the presence of lead-zinc mineralisation Thus no significance can be put on the values of this element in these dolostones when compared to the primary and secondary dolostone data given by Weber (1964) ie. whether these values indicate a primary or secondary origin.

7.2.4. Yttrium

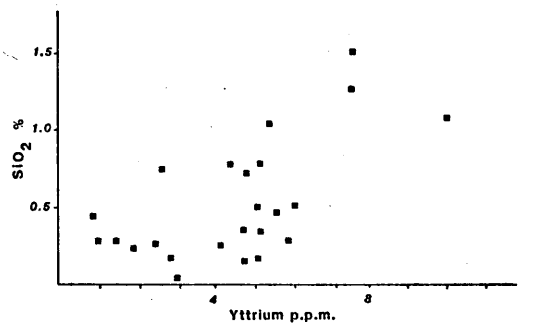


Figure 49 A plot of SiO_2 against the yttrium contents of the limestones

Although the yttrium contents of many limestone and dolostone samples are below the detection limits of the equipment, a positive correlation with silica occurs. Both the limestones (correlation coefficient = 0.51) and

dolostones (correlation coefficient = 0.99) show a fair correlation with silica (fig. 49) and suggests that yttrium is associated with the clay minerals.

7.2.5. Bromine

Bromine values for the limestones of this study are negligible and below the detection limits, yet the dolostones show consistently higher values, as indicated by the high correlation coefficient (0.82). This may reflect a rise in chlorinity, that would be associated with, for example, hypersaline dolomitising fluids, due to the similarities of the chemistries of chlorine and bromine.

Many of the traces noted above, apart from strontium have proved to be of little use in studying the origin of the dolomitising fluids. A more detailed geochemical study of the levels of lead, zinc and yttrium in the dolomite is required to gather some idea of the trace chemistry of the dolomitising brines.

7.2.6. Rare Earth Elements (R.E.E.)

Twelve whole rock limestone and dolostone samples together with separated calcite, dolomite and clays were analysed by Instrumental Neutron Activation using the procedure outlined in Appendix VII. The constituent dolomite, calcite and clay were obtained by controlled leaching experiments following the procedure outlined by Spirn (1965) (see Appendix VII). Briefly, this involved the dissolution of the limestone or dolostone in either acetic or nitric acid in the presence of E.D.T.A. and under strict pH conditions. The presence of E.D.T.A. during dissolution is believed to prevent the absorbtion of soluble rare earth elements by the clay component of the limestone or dolostone. The E.D.T.A. is believed to form complexes with the loosely bound R.E.E. on the surface of the clay thus preventing leaching.

The results of this study (fig. 50A) suggest that the presence of E.D.T.A during dissolution does have a significant effect. Dissolutions, both with and without the addition of E.D.T.A. were performed. In the leachates with E.D.T.A. the rare earth concentrations are generally lower than in the leachates obtained without the use of E.D.T.A. There is a corresponding rise in the rare earth concentration of the clay when E.D.T.A is present in the solution.

Only in the last twenty years have a significant number of studies been made of rare earth distributions in marine

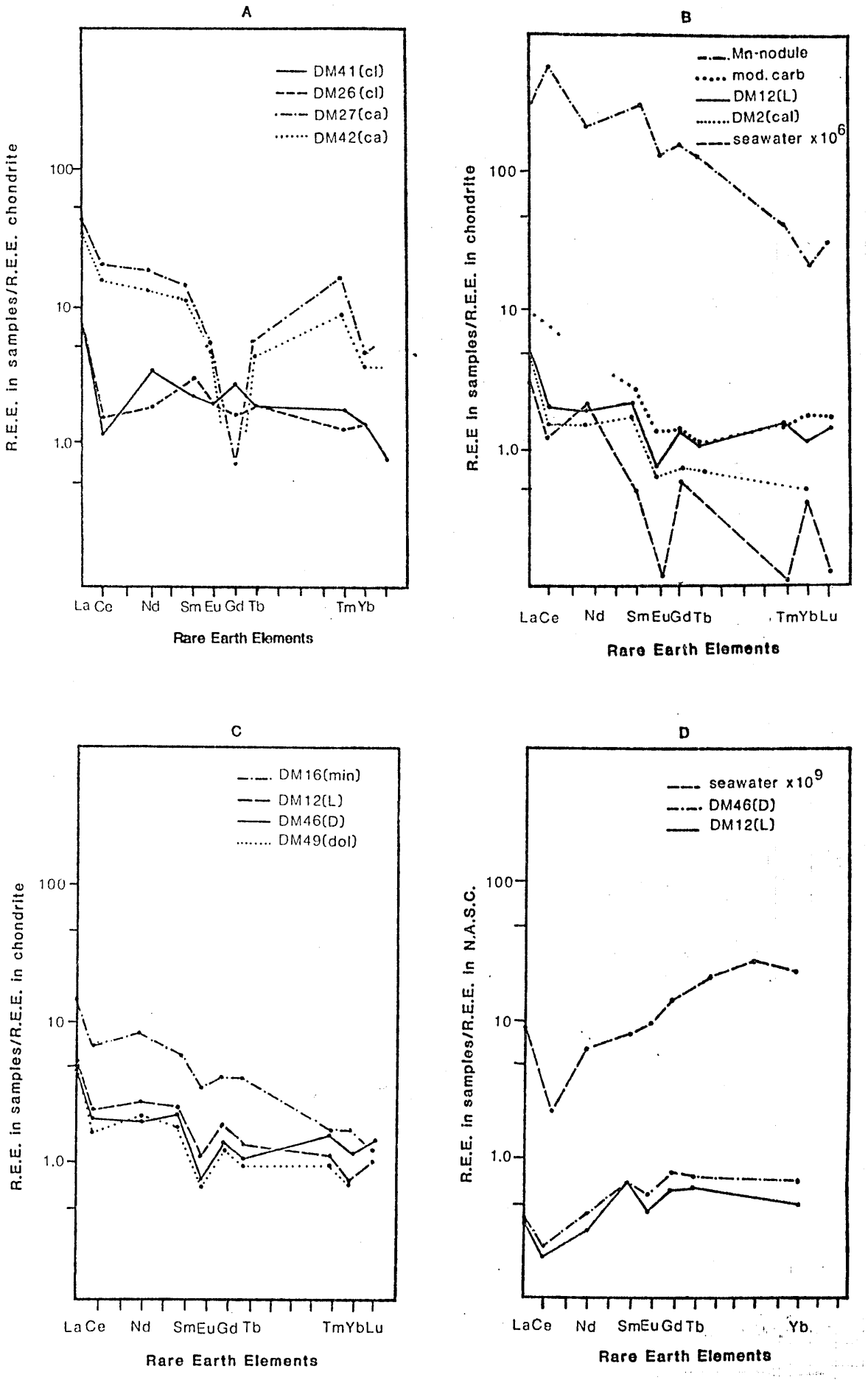


Figure 50 The rare earth distributions of the Wirksworth limestones dolostones, plus the distributions of their constituent calcite, dolomite and clays. L=limestone; D=dolostone cal.=calcite; dol.=dolomite; cl.=clay.

samples. Much of the earlier work involved the study of marine shales i.e. Minami (1935), Haskin and Geyl (1962), and Haskin and Haskin (1966) whilst, more importantly, in relation to this study Goldberg et al. (1963), Wildeman and Haskin (1965), Schofield and Haskin (1964) and Spirn (1965) began to study the individual marine phases. Little is known of the co-precipitation of rare earth elements in marine carbonates and the behaviour of these elements during diagenesis. Diagenesis is of particular importance in carbonates due to the extensive dissolution, recrystallisation and precipitation in these rocks. Parekh et al. (1977) analysed numerous carbonate samples but paid little attention to diagenesis. However, more recently Scherer and Seitz (1980) have begun to study the effect diagenesis has upon the rare earth distribution in marine carbonates. Certainly, any further extension of the study of rare earths in limestones must deal with the distribution of these elements in individual calcium carbonate phases. This must include the primary precipitates, biogenic carbonate and later low magnesium calcite either from the recrystallisation of early phases or precipitation in the active phreatic zone (Section 3.3).

(1) Limestones

The limestone rare earth distributions show marked cerium and europium anomalies (fig. 50B). Similar anomalies have been noted by Goldberg et al. (1963), Høgdahl (1966-68) and Piper (1974) to occur in seawater, and by Haskin and Geyl (1962), Parekh et al. (1977) and Scherer and Seitz (1980)

to occur in modern and ancient carbonates (fig. 50B). The cerium anomaly appears to be a distinct feature of open marine waters and carbonates precipitated from these waters. River water, such as the Gironde (Høgdahl 1966, 1968), and seawater of restricted seas, such as the Mediterranean, dominated by river water (Høgdahl 1966-68), and the Barents Sea, dominated by ice melt water (Piper 1974), show no cerium depletion.

Cerium within the oceans is more strongly fractionated relative to the other rare earths in response to its oxidation to the quadrivalent state. Parekh et al. (1977) noted that Ce^{4+} has a similar chemical behaviour to thorium. The removal of thorium is explained by absorption on suspended matter or by active scavenging of thorium by marine organisms. The same could cause a relatively fast removal of cerium (as Ce^{4+}) from seawater, thus lowering its residence time by a factor of 4, compared to the other rare earths. Cerium may also be lost due to direct precipitation of the Ce^{4+} or to the co-precipitation of Ce^{4+} with iron and manganese hydroxides in, for example, manganese nodules. Goldberg (1963) has shown that the manganese nodules have positive cerium anomalies (fig. 50B) and may act as an efficient sink for the cerium.

The europium anomalies are a function of the rocks weathered at the earth's surface. Many writers have shown the upper crust to be deficient in europium. If the rare earth element abundance of seawater is normalised to the North American Shale Composite (N.A.S.C.) (fig. 50D) then no anomaly can be seen, indicating its inheritance from the former rocks of the upper

crust. Jakes and Taylor (1974) considers this depletion to be a consequence of the development of the granodioritic upper crust by partial melting in the lower crust which selectively retains europium. These limestones, however, appear to have slightly greater europium anomaly even when normalised to shale. Care must be taken when considering these data as the size of this anomaly is not really significant.

(2) Dolostones

The dolostone rare earth element distributions are very similar to those found in the limestones (fig. 50C), again showing very distinct Ce and Eu anomalies. No significant difference between the Ce and Eu anomalies of the limestone and dolostone can be seen. This suggests that either (1) the dolostones were precipitated from seawater under similar conditions to those during deposition of the lime muds; or (2) the rare-earth distributions have been inherited from the former calcite or (3) the rare earth concentrations in the fluids were different but the conditions prevailing during dolomite formation caused the development of a similar rare earth distribution to that in the limestones.

No evidence for the deposition of dolomite from normal seawater has been found and it seems unlikely, although indeed not totally impossible, that the conditions may have been such as to produce a similar distribution to that of the limestones. The likeliest explanation is that the rare-earth distribution has been inherited from the calcite (original limestones) at the site of dissolution - reprecipitation.

In Section 7.3., four possible origins for the dolostones are discussed, these are deposition from; (1) hypersaline brines, (2) brackish waters (3) connate brines or (4) hydrothermal waters. In each of these cases precise determinations of rare earth distributions developed in these environments is difficult due to the lack of knowledge of the conditions, such as temperature, Eh and pH, prevailing during dolomite formation.

Hypersaline brines might be expected to be magnesium rich yet depleted in rare earths. Precipitation of calcium carbonate and sulphate in the evaporating waters would cause a rise in the Mg : Ca ratio, and a corresponding depletion of the rare earths due to their high partitioning into calcium carbonate (Parekh et al., 1977). A magnesium rich R.E.E.-poor solution may well give rise to the R.E.E. distribution found in the dolomite The R.E.E.- nature of the solution would allow the rare earth chemistry of the dissolving calcite to dominate the precipitating solution, thus allowing a regeneration of the former calcite distribution. However, it is not known what effect the adverse conditions in those evaporating waters would have upon argillaceous material present, that is, whether rare earths could be introduced into these waters by leaching of the clays.

In brackish waters, mixing of seawater and saturated groundwater, mainly derived from the dissolution of local carbonate by meteoric water has been shown by many writers to cause dolomitisation (Section 7.3.2.(a)) Scherer and Seitz

(1980) have shown that low magnesium calcites, deposited from calcium carbonate-saturated groundwater, are only slightly depleted in rare earths. Thus, if dolomitisation occurs in these waters (Section 7.3.2(a)), then again a similar rare earth distribution to that in the limestones, would be developed in the resulting dolostones.

The rare earth concentration of connate brines is difficult to assess due to the lack of information concerning their formation and the variability of the conditions existing in these waters.

The character of the hydrothermal solutions which produced the widespread lead-zinc mineralisation associated with these dolostones, can be found from an analysis of the gangue calcite. This can be seen to be relatively enriched in rare earths (fig. 50C) and consequently appears unlikely to have given rise to the rare earth distribution found in these dolostones.

Thus, the Rare Earth Element distributions of these dolostones cannot clearly differentiate between the numerous origins for the dolomitising fluids. Although, from the discussion above, it has been shown that seawater has played a significant role during dolomitisation.

(3) Mineralisation

Figure 50C shows the gangue calcite of the mineralisation to be highly enriched in rare earths, but shows similar cerium and europium anomalies. The presence of these anomalies

suggests that much of the calcium carbonate of the gangue has been supplied by the dissolution of local limestone. The original fluid must have been fairly enriched in rare earths prior to the dissolution of the limestones. This rare earth enrichment may have been even greater closer to its source as indicated by Moller et al. (1979) in the Harz Mountains. The deposition of different mineral phases such as fluorite, barytes and the numerous sulphides will have significant affect upon composition of the original fluid as these phases are enriched in R.E.E., and thus effectively reduce the R.E.E. concentration of the mineralising fluids.

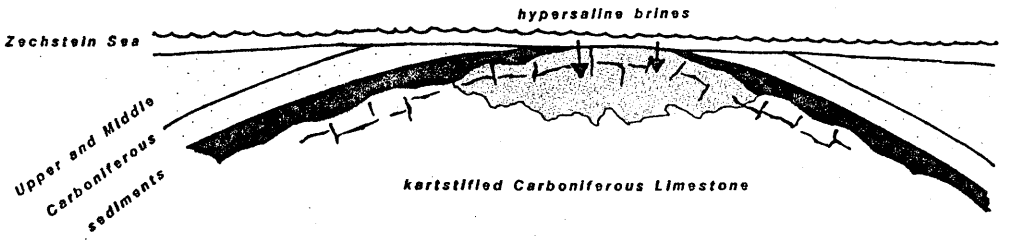
The most popular theories for the origin of the Derbyshire mineralisation are outlined in Chapter VI. Briefly these are: from a granitic source to the east of Derbyshire, the presence of which is not proven; and from the remobilisation of salts from Triassic sediments. If the limestone constituent of the gangue calcite is removed then the resultant fluid has a slight positive europium anomaly, which is characteristic of some gabbro-diorites. However, no other evidence, for example gravity or aeromagnetic, for such a body, has been found.

7.3. The Origin of the Dolomitising Fluids

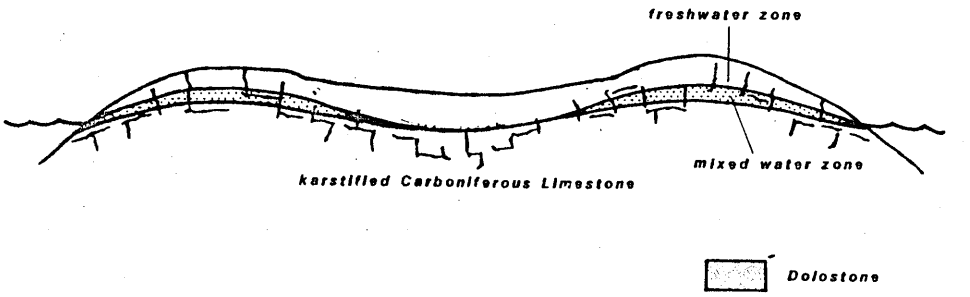
The aim of the above geochemical study was to gather some idea of the chemistry of the dolomitising fluids and hopefully identify their origin. The following section is a summary of the various models discussed in the literature and also a discussion of which, if any, of these models is reflected in the geochemistry of the dolostones. The conclusions reached are inconclusive as the discussion is intended to broaden ideas concerning the origin of the dolostones in Derbyshire, rather than present a single model, at this early stage in the study of the thermodynamics of dolomite. The relative dearth of information in the literature concerning the thermodynamics of dolomite has led to a great deal of conflicting information appearing in the literature. The problem lies in the difficulty of synthesising dolomite in the laboratory under conditions that are similar to those found in sedimentary environment. Thus, the published data are mainly circumstantial and based upon field data and comparable data for calcite. At present, most information can be given by the study of calcium, magnesium, iron, manganese, sodium, strontium and possibly the rare earth elements.

As early as 1914, Van Tuyl discussed a number of ideas in relation to the origin of dolomite and this was furthered particularly in respect to ore deposition by Hewett (1928).

1.Hypersaline Model



2(a)Mixed Water Model



2(b)Connate Brine Model

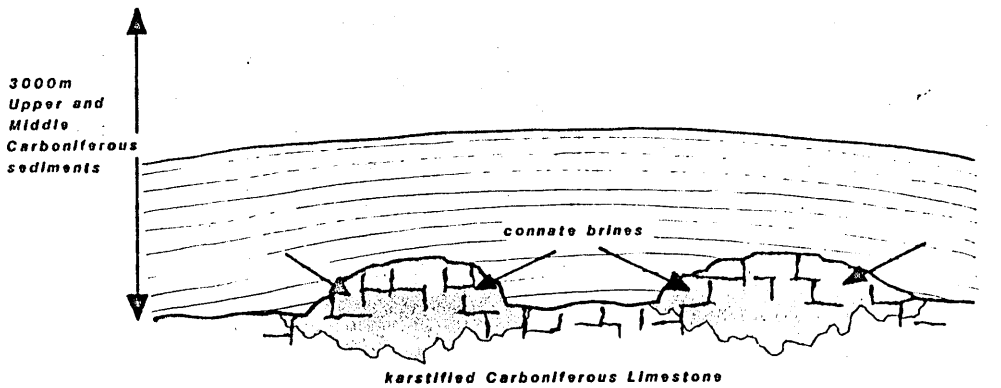


Figure 51 Diagram of the various modes of origin for the Wirksworth Dolostone; (1) the hypersaline model, (2a the mixed water model and (2b the connate brine model.

More recently, good reviews of modern ideas are given by Fairbridge (1957) and Friedman and Sanders (1967). The most notable and highly endorsed origins, which were included within the Van Tuyl paper, are (i) deposition or alteration by marine hypersaline brines, (ii) alteration by groundwater both mixed water (brackish) and connate and (iii) alteration by hydrothermal waters.

7.3.1. Hypersaline Brine Model

Dolomitisation caused by magnesium-rich hypersaline brines, in lagoonal, lacustrine or marginal marine environments, has become the most popular model in recent years, and was endorsed by Friedman and Sanders (1967). The dolomite occurs both as primary precipitates shown by Von der Bosch and Jones (1976) to be occurring in the Coorong, S.E. Australia, or more frequently by the alteration of previously deposited carbonate sediment. The popularity has arisen from the discovery of dolomite in modern environments by Alderman and Skinner (1957) in the Coorong, Peterson et al., (1963) in Deep Springs Lake, California, Deffreyes et al (1965) in Bonaire, Dutch Lesser Antilles, Illing et al., (1965) and Kinsman (1965) in the Persian Gulf and Shinn et al., (1965) in the Bahamas. The brines are characterised primarily by a very high Mg/Ca (weight percent) ranging from 5:1 up to 100:1 with total salinity rising as much as five times that of sea water. Both the high magnesium/calcium ratio and high salinity are thought to be prime controlling factors.

to cause dolomitisation. Other common features of the environment are high pH (8-10 Alderman and Skinner 1957), low Eh (though variable) and low carbonate content, accounting in part for the much higher pH. The dolomites formed as a result of these brines are often non-ideal, termed "proto dolomite" (Graf and Goldsmith 1958), ie. not showing the distinct magnesium and calcium layering of the lattice. Instead the protodolomites are calcium-rich, the calcium ions replacing Mg ions within the magnesium layers. Many authors have attributed the non-ideal nature and fine crystal size of modern dolomites, to rapid crystallisation in these highly saline conditions (Folk and Land 1975). However, well-ordered dolomite has also been found associated with these brines (Alderman and Skinner 1957 and Peterson et al., 1963) and are thought by Alderman and Skinner in Coorong, to be due to much higher Mg/Ca values.

The theory of hypersaline brines originating in an extension of the Zechstein Sea Basin across the Southern Pennines, and slowly percolating downwards into the exposed Carboniferous Limestone (Dunham 1952), has been the principal model presented for the origin of the dolostones of the Wirksworth area (fig. 51). Ford (1967) has been a strong advocate of this model and believes that the Upper Carboniferous deposits, removed by erosion in the early part of the Permian due to the upwarping of the Pennine anticline, allowed exposure of the underlying limestone. Evidence of this exposure in early Permian is sparce, with limestone and chert pebbles occurring in a Permian pebble bed in Warwickshire, Certainly, extensive exposure had occurred by the Triassic as shown by the abundance

of limestone and chert in the Bunter Pebble Bed.

The dolomitisation is believed to have been caused by the seepage of evaporitic hypersaline brines, enriched in magnesium, due to the precipitation or either aragonite or high magnesium calcite and gypsum. No evidence for this transgression can be found although Kent (1957) supports such a transgression. Indeed a projection of the base of the Triassic around the area only gives a position about 100ft above the present-day limestone massif, suggesting that the plateau structure of the dolostone area, occurring at 900ft-1100ft, may be related to a former peneplain. However, evidence from the south of the area suggests that a considerable relief may exist below the Triassic unconformity (Clayton 1953) although Kent (1957) argues against this idea. However, Pitty (1968) considering the present rate of dissolution, believing this to be mainly surface lowering from the relative lack of karst features, calculates that approximately 1000m of limestone may have been lost during the last 20 million years. Also much of the present day drainage pattern found in the Peak District is related to the uncovering of an impermeable cover (Edale Shales) and not related to the structure of the Dome. Thus, the limestone may have been unroofed quite recently. Walsh et al (1972) have indicated that during the Lower Pliocene the southern part of the Derbyshire Dome was covered by at least 21 metres of shale some 150m to 250m above the present day surface. They also added that this shale

capping may not have been complete thus, allowing dolomitisation. But perhaps the real question to ask is whether the chemistry of the dolostones reflect dolomitisation by hypersaline brines?

The CaO/MgO, Fe_2O_3 and Mn^{2+} values found in the dolostones could all be accounted for if we consider dolomitisation by hypersaline brines. As stated the good stoichiometry seen in the dolostones has been found in connection with modern hypersaline brines. The iron and manganese contents of the dolostones are comparatively low and can easily be accounted for in hypersaline brines due to the low Eh and reducing conditions, making available abundant Fe^{2+} and Mn^{2+}. Most recent work has involved the use of sodium and strontium as palaeosalinity indicators. The sodium values of these dolostones (Section 7.1.1) have a mean of 267.8 p.p.m. Veizer et al (1978) give a value of 230 p.p.m. to divide open marine from hypersaline conditions and this is in good agreement with Fritz and Katz's (1972) value of 200-700 and Randazzo and Hickey's (1978) value of 916 p.p.m. (Section 7.1.4.) for supratidal dolomite. The values of the Wirksworth dolostones only just fall within the hypersaline range. From published data especially the work of White (1978) a truely hypersaline brine would be expected to give higher sodium values, perhaps 500 p.p.m. Thus the sodium values appear at odds with this mode of origin.

Even taking into consideration the variability of data on strontium partition coefficients in the literature, strontium

serves as a remarkably efficient tool to study diagenesis. The strontium values of these dolostones are very low (av. 59.7 p.p.m.) and as shown in Section 7.2.1. represent either strontium-depleted or calcium-enriched solutions. Neither of these conditions are satisified when considering hypersaline fluids. The precipitation of calcium carbonate and calcium sulphate which gives the magnesium enriched brines causes a relative decrease in calcium concentration and increase in the mSr^{2+}/mCa^{2+} of the fluids, due to the K_{Sr}^{calc} and K_{Sr}^{gypsum} being less than unity (0.14 Kinsman 1969 and 0.21 - 0.64 Kushnir 1980, respectively), and a decrease in the calcium content. These lower values of Na^{+} and Sr^{2+} suggest that recrystallisation may have occurred involving sodium and strontium deficient solutions such as meteoric water. There is no positive evidence to suggest whether or not dissolution-reprecipitation has taken place. However, if recrystallisation has occurred then it seems strange that fossils and textures, such as varying crystal sizes, and zoning have survived. Also the Sr^{2+} values are extremely low if we involve an hypersaline condition. Thus, to account for these low Sr^{2+} values, considerable mixing with meteoric waters has to be involved, in which case much lower values of Na^{+} would be expected.

Another quite significant feature of this hypersaline environment is the lower carbonate content (0.1% Alderman and Skinner (1957). Usdowski (1968) notes that a Cl^{-} rich, CO_3^{2-} poor, dolomitising fluid causes a molecule for molecule replacement to occur. The dolostones of this study have been shown to have been replaced volume for volume (Section 5.2.).

It can be argued therefore that in fluids of low carbonate concentrations, sufficient fluids would have to pass through the carbonate to give a volume for volume replacement. The incomplete dolomitisation of crinoidal fragments may testify to a carbonate deficient solution, the crinoidal fragments remaining resistant in the early stages of dolomitisation and possibly dissolved at a later stage to provide the much needed carbonate ions.

7.3.2. Groundwater Models

The composition and evolution of groundwater is both variable and complex. At shallow depths meteoric water is dominant and is rich in carbonate and sulphate. At much greater depths such a those encountered in oilfields, connate brines representing "fossil" seawater are much richer in sulphide. These connate brines can be both hypersaline and less saline waters (Degen and Chilingar 1967). Certain conditions and environments exist where dolomitisaion can occur in these ground water zones. Recently a popular idea has been the mixing of normal marine waters or hypersaline brines with fresher water (mixed water zone) which will allow the slow development of dolomite. Similar conditions may exist where connate brines of different salinities mix at depth, although many of these connate brines are hypersaline and at depth can give suitable conditions to induce dolomitisation.

7.3.2. A Mixed Water Model

In the last fifteen years this mode of dolomitisation

has become widely recognised. In a mixed water environment such as occurs in coastal areas. The mixing of fresh water and sea water can occur in a number of instances involving either normal marine or hypersaline (schizohaline zone Folk and Siedlecka 1974) waters. In this model the dolomite is characteristically much coarser and commonly described as "limpid" (Ford and Siedlecka 1974 and Weaver 1975) ie. very clean, stoichiometric euhedral dolomite. This a great contrast to that reported from hypersaline areas where the dolomite is characteristically finely crystalline and has a poorly ordered lattice.

The idea of dolomitisation caused by the mixing of marine and freshwater is not a modern concept, it was originally included in the work of Collegno in the 18th century and by Steidtmann (1911). The idea gathered momentum due to the work of Hanshaw et al., (1965, 1971) in the Florida and Yucatan Peninsulas, where it was believed that sufficient magnesium may be supplied in the mixed water zone by marine waters. Land (1967) indicates that although the Mg/Ca is important during dolomitisation the higher values may not be necessary for dolomitisation to occur, but do induce more rapid crystallisation. Hanshaw et al., (1971) after studying various formational waters in the carbonate formations of the Florida and Yucatan Peninsulas concluded that a mMg^{2+}/mCa^{2+} greater than unity in active groundwater may cause slow dolomitisation. This slow crystallisation is believed to allow the formation of well-ordered, euhedral dolomite (Weaver 1975). Badiozamani

(1973), furthered the work by suggesting a means by which the reaction occurred. A mixture of 95 percent meteoric groundwater and 5 percent ocean water can be shown to be undersaturated with respect to calcite, due to the non-linear nature of the solubility of calcite. The mixing of two waters, both saturated with calcite, but having different concentrations, would form a solution which was undersaturated with respect to calcite (Runnells 1969). However the mixture of ocean and meteoric ground waters will remain supersaturated in dolomite, thus allowing dolomitisation to occur. In fact it is shown that a mixture containing as much as 30 percent ocean water could cause dolomitisation in this manner. Sufficient carbonate material is readily available from the groundwater and ocean water to allow complete dolomitisation (Usdowski 1968). Badiozamani termed this the "Dorag" model (mixed blood). The arguement was supported by a study of the Mifflin Dolostone, Wisconsin, giving a good opportunity to compare its chemistry with the dolostones of this study. The low sodium (190 p.p.m.) and strontium values of the Mifflin dolomite are attributed to the mixing of sodium and strontium deficient meteoric water. The oxygen and carbon isotopes also show the dominance of a freshwater phase. Folk and Siedlecka (1974) found examples of dolomitisation in this mixed zone at Bear Island, Svalbard, but mixing of fresh-water with hypersaline waters occurs. The zone of dolomitisation alternates between fresh and hypersaline waters (schizohaline) with limpid dolomite forming in the fresher environment with a mCa^{2+}/mMg^{2+} close to unity. The most mentioned paper

is that of Folk and Land (1975) although outlined as an abstract in 1972. The writers believe salinity to be the controlling factor during dolomitisation. In the mixed water zone a reduction of salinity occurs yet maintaining the high Mg/Ca of ocean water. The crystallisation rate is reduced due to the lower concentration, with less interfering ions which allow the growth of well-ordered dolomite from fluids with mMg^{2+}/mCa^{2+} ratios as low as 1 : 1. Randazzo and Hickey (1978) attributed limpid dolomite in the Florida Aquifer with its low strontium level (88 - 190 p.p.m.) to dolomitisation by less saline brackish water. Thus sufficient evidence exists in the literature to establish the model as a major contributor to the dolomite problem. Carpenter (1976) challenges the Badiozamani model, although it is equally applicable to the Folk and Land model. In the marine environment, the hydration of magnesium inhibits the formation of dolomite. It has been found that at higher salinities hydration is reduced, and thus in low salinities the development of dolomite must be furthered inhibited. Thus for dolomitisation to occur at these reduced salinities, the rate of crystallisation must be significantly slower, due to the availability of magnesium ions.

The geochemistry of the Wirksworth dolostone is rather contradictory. The iron and manganese contents are a poor indication of environment, as much higher iron and manganese contents in solutions may be brought about in many waters

including stagnant groundwaters. The mCa^{2+}/mMg^{2+} of the dolomite indicate a well-ordered stoichiometric structure (Table VI) such a distinct characteristic of this environment. However, well-ordered dolomite has been found associated with hypersaline brines (Section 7.3.1.). When discussing these models geochemically, it is the strontium and sodium which prove most useful. The strontium values (averaging 59.7 p.p.m.) are in close agreement with values given by Badiozamani (37p.p.m.) for the Dorag model, and thus by analogy indicate that the dolomitising fluids are strontium deficient as are meteoric waters (Section 7.2.1.). On the other hand the sodium values (averaging 267.9 p.p.m.) are much higher than those of Badiozamani (averaging 190 p.p.m.) and indicate saline fluids and not a mixed-water type (White 1978). Land et al., (1975) also invoked a mixed water zone model for a number of dolostones. Geochemically their dolostones are very similar to the Wirksworth dolostones especially with respect to strontium (90 p.p.m.) and sodium (300 p.p.m.). These sodium values indicate more saline conditions, although Land et al., argue that these sodium values are much lower than modern carbonates (600 - 4000 p.p.m.) and thus represent a mixing of less saline meteoric water during dolomitisation. White (1978) suggests that these much higher values for sodium in modern carbonates are a consequence of biogenic material. The experimental results presented by White suggest that 300 p.p.m. sodium would suggest quite saline conditions, probably hypersaline, in agreement with Fritz

and Katz (1972) and Veizer et al (1977). However, if this sodium content of 300 p.p.m. does represent biogenic limestones then possibly a dilution by meteoric water may be invoked. The strontium values are comparable to those of Badiozamani. A number of occasions have arisen where mixed water conditions could have occurred in the limestones of the Wirksworth area as well as the remainder of the Lower Carboniferous Limestone succession of the Derbyshire Dome. At the end of the Lower Carboniferous and in the early Permian subaerial exposure occurred (Ford 1964) and this allowed ample opportunity for a mixed water dolomitisation to occur. However, mixed-water conditions might be expected to give a quite widespread and continuous area of dolostone especially in a quite uniform limestone succession, where few local variations occur. This is not evident in the Wirksworth area where more localised dolostone outcrops occur (figure 5).

7.3.2. (b) Connate Brine Model

Little attention has been given to the possibility of dolomitisation occurring at depth, due to constantly changing connate brines. Examples of dolomitisation caused by magnesium-rich fluids, emanating from compacting clays (Rittenhouse 1949) or produced by the leaching of chlorite and magnesium rich clays (Freeman 1972) are rare in the literature. Al-Hashimi (1971) has also shown that the

iron-free dolostones of Northumberland were formed by magnesium-rich groundwater.

Many highly saline connate brines (chlorinity 19,000 - 200,000 mg/l) represent modified sea water, trapped in the sediments since deposition. Burial has caused a general loss of Mg^{2+}, HCO_3^- and SO_4^{2-} and a gain in Ca^{2+} and Cl^- during diagenesis (White 1957, Chave 1960, and Downing and Howitt 1969). The relative loss of magnesium is generally thought to be caused by the formation of dolomite and chlorite (White 1957 and Chave 1960) as well as illite and montmorillonite (Kaplin et al., 1963). The sulphate ions are believed to be lost by the deposition of gypsum or anhydrite and the presence of sulphate reducing bacteria. The loss of bicarbonate during burial may be due to the clays acting as filters, retaining Ca^{2+} and Cl^- and losing Na^+ and HCO_3^-. This salt-sieving was first recognised by Russell (1933), being caused by negatively charged clays restricting the movement of anions, which hold cations. This mechanism was later endorsed by De Sitter (1947) for producing the highly saline brines. Russell (1933) also included many other means by which the concentration may occur, such as osmosis, adsorption, hydration of clays, osmotic pressure and concentration by evaporation of gas. But it is the salt-sieving mechanism that has received most attention.

Although most connate brines are relatively Ca^{2+} rich examples of magnesium-rich brines have been reported by Downing and Howitt (1969) in the E. Midlands and in Northumberland by Al-Hashimi (1971). Magnesium enrichment is thought

to have been caused by a similar salt-sieving mechanism, without the loss of magnesium through dolomitisation and chlorite formation in the Lower Coal Measure waters (Downing and Howitt 1969). Al-Hashimi (1971) proposed that the base exchange property of clays exchanging cation for cation could increase the magnesium content and account for dolomitisation in Northumberland. Magnesium would replace Ca^{2+} in solution, as the calcium content rises this would activate the ion exchange mechanism. Bicarbonate rich waters may also attack Mg-rich clay minerals and liberate magnesium.

Therefore, there is the possibility of relatively magnesium enriched brines occurring at depth and similar brines have been found close to the study area (Downing and Howitt 1969). However, Usdowski (1968) has shown that at temperatures of $80^{o}C$ and waters having 18 mol. % Mg dolomitisation can occur. This magnesium level can be found in most published analyses of connate brines. Most brines vary between 0.17 and 0.85 Mg/Ca ie.8 - 43 mol% Mg and thus if a temperature of $80^{o}C$ exists then dolomitisation will occur in the majority of cases. This leads to a problem, in that dolomitisation is only localised and due to the mol.% Mg of most brines, one would expect dolomitisation to be more widespread, thus it seems likely that other factors influence dolomitisation. De Sitter (1947) has pointed out that connate waters in the Arbuckle Limestone have relatively lower chlorinities also White (1957) found waters with lower Ca/Mg and salinities.

These may be a consequence of the non-compacted nature of the limestone and remnant freshwater from periods of sub-aerial exposure. This may explain to a certain degree the non-dolomitised nature of many limestones.

The presence of less saline water in the limestones, either remnant or produced by compaction within the shales (expulsion), allows mixing with hypersaline connate brines from adjacent shales and may allow dolomitisation to occur within the limestones in a similar manner to that suggested by Folk and Land (1975), giving stoichiometric dolomite due to the slow rate of crystallisation (Section 7.3.2(a)). A problem with dolomitisation in the presence of connate brines is the lack of carbon ions. This gives difficulties when considering a volume for volume replacement (Usdowski 1968) and would require quite active movement of brines to supply sufficient carbonate. However, the less dolomitised hypidiotopic and idiotopic dolostones may indicate the ineffectiveness of some fluids to cause complete dolomitisation and may reflect a carbonate deficient fluid. Some carbonate material may be introduced by the decay of organic matter or the oxidation of hydrocarbons by mineralisation. Carbonate-rich water may be supplied by the carbonate formational waters and thus could play a significant role when mixed with connate brines from overlying shales. A rise in the carbonate ions may induce dolomitisation, due to the dehydration of magnesium at higher carbonate concentration (Davies et al. 1977).

Thus where limestone is underlain or overlain by shales, there is the possibility of hypersaline connate brines, possibly magnesium-rich emanating by compaction, becoming mixed with the less saline, carbonate rich waters of the limestones which may give rise to any area of dolomitisation.

In view of the state of geochemical knowledge concerning the connate brines and dolomitisation, the Wirksworth dolostones could easily have formed in one of these connate brines, due to the great variations of these brines reported and the lack of understanding concerning the dolomitisation process. The sodium value (av 267.8 p.p.m.) of the Wirksworth dolostones are much higher than would be expected, considering the much lower mNa^{+}/mCa^{2+} of many published analyses of connate brines. Seawater has a mNa^{+}/mCa^{2+} of 46 and gives a sodium p.p.m. in inorganically precipitated calcite of less than 200 p.p.m. no greater fractionation of Na^{+} in a dolomite is expected following the experimental work of White (1978). Most connate brines have much lower mNa^{+}/mCa^{2+} ratios ranging from 5 - 44 (Chave 1960, Schmidt 1965, and Downing and Howitt 1969) and thus under surface conditions would give a sodium concentration below 200 p.p.m.. Isolated high mNa^{+}/mCa^{2+} (67) have been reported and under these conditions dolomitisation could produce dolomites with similar sodium contents to those found in this study. If dolomitisation is to occur associated with the generally lower mNa^{+}/mCa^{2+}

ratios then a greater partitioning of sodium has to occur. This may be caused by a rise in temperature, but White (1978) gives no indication of the effect of temperature as in his experiments the temperature remains constant at 25°C.

Strontium values are less problematical than sodium considering present-day knowledge of strontium chemistry. The published partition coefficients of strontium in calcite are variable, but less so at higher temperatures which will be associated with these brines are depth, 0.07 (Kinsman) and 0.058 (Katz et al., 1972) for 100°C. When considering dolomite the partition coefficients are taken as being 50% that for calcite (Section 7.2.1.). Published strontium data of connate brines are limited and the mSr^{2+}/mCa^{2+} varies between 1.5 and 3.7×10^{-2}, which means the connate brines are relatively enriched in strontium due to the dissolution of Sr^{2+} rich carbonates such as aragonite, or Sr minerals such as strontianite or celestine (Sass and Starinsky 1979). These much higher mSr^{2+}/mCa^{2+} values would give strontium contents in dolomite of between 454 and 1225 p.p.m. considering the variability of the partition coefficients and and published strontium data. This assumes a similar pH to that of seawater which is also found in most connate brines. These Sr^{2+} values are far in excess of those found in the Wirksworth dolostones . Badiozamani (1973) as indicated that the strontium levels in calcite will decrease with increasing calcium concentrations (Section 7.3.1.). The calcium concentrations in connate brines are in many cases a hundred times

greater than normal seawater. The increase would cause a corresponding fall in the strontium values and thus give ranges of strontium values, certainly within the realm of the strontium data obtained from the Wirksworth dolostones.

The relatively low iron and manganese contents are easily explained by the iron and manganese concentrations of 10 p.p.m. iron and 1 p.p.m. manganese (White 1957) commonly found in connate brines.

In the Derbyshire Dome the Carboniferous Limestone is believed to have been overlain by Middle and Upper Carboniferous sediments. The Middle Carboniferous (450 metres) and Upper Carboniferous (1200 metres) may have developed to a thickness of approximately 1800 metres in this southern part of the limestone outcrop, though much larger thicknesses have been noted further north (Spink and Ford 1968). At depth below this thickness of sediment a temperature of 70 - 80°C might be expected and thus would require a 18 - 20 mol. % Mg to cause dolomitisation (Usdowski 1968) which can be easily be accounted for in many connate brines. (fig. 51).

The top of the Carboniferous Limestone is marked by a significant unconformity, Ford (1964) reported that during this period of subaerial exposure a relief in excess of 500m was developed and associated with extensive karstification. This karstification would allow good lateral access for hypersaline connate brines emanating from the flanking Edale Shales (fig. 51). Examples of the limestone protruding

into the shales due to this palaeorelief are given by Chrome and Parkhouse Hills which are surrounded by the Edale Shales. This could explain the very localised distribution of the dolostones, occurring at the "1,000 ft Plateau", which reflects an earlier palaeokarstic surface. This palaeokarstified relief presents an ideal situation for the possible mixing of hypersaline and less saline, carbonate rich waters from the carbonate formation mentioned in the above discussion.

7.3.3. Hydrothermal Models

The possibility that mineralisation supplied the necessary fluids for dolomitisation in Derbyshire was suggested by Ford (1968). On account of the abundance of lead - zinc mineralisation, associated with the dolostone outcrop (Section 6.2.). A hydrothermal origin for dolostones has always been prominent and was the subject of an excellent review by (Hewett 1928). Since Hewett (1928) dolostone has been found associated with ore deposits of the Mississippi Valley type and associated with undoubtedly hydrothermal ore deposits in the Rocky Mountains and in Europe. In most of the districts where the limestones have been altered near ores, the chief metals mined are lead and zinc. Away from the walls of mineral veins, evidence of a hydrothermal origin for dolostone is rare, and since the discovery of dolomites in the modern marine environment, has received little attention. To explain the origin of the magnesium in these hydrothermal solutions , five sources were suggested by Hewett viz.

(1) seawater (2) the shell of sedimentary rocks (3) underlying crystalline rocks (4) shallow bodies of intrusive rocks and (5) deeper magmas. Under the temperatures thought to have been present during the deposition of these minerals in the Wirksworth region i.e. 180°C (Ford 1968), dolomitisation could easily be caused by any of the above waters. A popular theory for dolomitisation and the mineralisation is the activation of magnesium-rich connate waters (similar to those described in Section 7.3.2(b)) by nearby intrusives. The heat from these intrusives causes the initiation of convection cells allowing the activation of these brines. The metal elements may be provided by the intrusive body or the brines. Another mode, and particularly important when considering the Mississippi Valley deposits, is that of Jackson and Beales (1967). They have suggested that many of these lead-zinc deposits may have originated from the mixing of fluids rich in metallic elements emanating from shales and sulphide-rich waters commonly associated with carbonate formations (Section 7.3.2(b)).

In the Wirksworth area the presence of an intrusive body to the east has been suggested but never proven (Section 6.2). The idea of Jackson and Beales (1967) has similarities to the origin discussed by King (1968) involving the leaching of metallic salts from the Triassic sediments. Section 7.3.2(b) discussed the possibility

of the dolomitising brines originating from the compacting Edale Shales and this certainly has strong parallels with the Jackson and Beales idea.

Geochemically the gangue calcite of the mineralisation found in the study area is quite distinctive from the limestones and dolostones, although as the rare earth elements show (Section 7.2.6), much of the carbonate must have been supplied by local carbonates. In comparison to the dolostones, the mineralisation shows an increase in strontium, lead and zinc and a decrease in iron and manganese. The rise in strontium and possibly the fall in iron and manganese may be explained by the different partition coefficients occurring between calcite and dolomite for these elements (Sections 7.1.5 and 7.2.1), and other factors such as temperature and pH will affect the concentrations markedly. However, the lead and zinc values suggest that the mineralising solutions were relatively enriched. The rare earth elements also show a similar enrichment (figure 50) which cannot be explained by differences in partitioning especially at these raised temperatures. These enrichments indicate that the dolostone and mineralisation were not precipitated from the same solutions, but the similarities especially Sr^{2+} may suggest they have related origins.

Considering the fact that the rare earth elements' distribution suggests a local source of calcium carbonate,

for the gangue calcite, and given the localised nature of the dolostone, a comparison of the limestone and gangue calcite may give an indication of the mineralising fluids' source, i.e. any change in the chemistry of the calcite must have been introduced by an extraneous source. The mineralisation seems to show a rise in iron, manganese, lead, zinc and the rare earth elements, but a fall in the strontium value.

Connate brines as shown in Section 7.3.2(b) could supply fluids relatively enriched in iron and manganese, yet deficient in strontium. The dolostones show no enrichment in lead and zinc and the occurrence of these in the connate brines was not discussed although an enrichment of these elements in connate brines was suggested by Jackson and Beales (1967). Unfortunately, the usefulness of rare earth elements as indicators of this type of water is limited due to the inadequacies of their study (Section 7.2.6), although it is likely that a concentration of the rare earth elements may occur in interstitial waters of shales, due to the presence of weakly bonded ions on the surface of clays (Section 7.2.6). It is unlikely that leaching of granitic rocks, in convection plumes produced by their own heat, has caused rare earth element concentration, as sericitisation should cause little concentration of rare earths (Alderton et al. 1980). This does not preclude the possibility that the granitic rocks provided the necessary mobilisation of formational waters causing mixing of different types of waters as noted by

Jackson and Beales (1967), although sufficient mobilisation may have been provided by compaction, which causes expulsion.

Thus, the dolostones can be shown not to be directly associated with the mineralising solutions, although some similarities in their strontium, iron and manganese contents exist. If, the dolostones and mineralisation are assumed to represent different phases of the same process then a great concentration of certain metals has occurred. The two phases have been separated by a phase of karstification which is probably related to sub-aerial weathering (Ford (1964), although King (1968) does express the view that karstification may also be related to a phase of mineralisation. Whatever the origin of the karstification may be, the chemistry of the fluids has changed quite drastically after karstification, providing metallic enriched solutions. This may represent, as suggested by King (1968), leaching of these elements from the Triassic sediments (Section 6.2).

7.4. Conclusion

As stated at the beginning of this discussion the aim of the study has been to extend and discuss both old and new theories concerning the origin of the dolomitising fluids. None of the modes of dolomitisation discussed acquired a favoured status from the chemical data. The hypersaline model although supported to some extent by

the high sodium contents, does not explain the low strontium values. Contrastingly, the mixed water or brackish water model shows a good agreement in its geochemistry except that the sodium values appear too high. The hydrothermal model seems unlikely due to the fact that the calcite has a relative enrichment of lead-zinc and rare earths but the dolomite has not. The model which best fits the limited evidence involves a connate brine. There is good agreement between the chemistries of published connate brines and those of the dolostones. Again the high sodium contents appear a little anomalous, although mNa^{+}/mCa^{2+} rich fluids have been found.

The R.E.E. give no conclusive proof for the origin of the dolomitising fluids. A full discussion of the use of R.E.E. in recognising different dolomitising solutions is given in Section 7.2. Briefly, the enhanced concentration of the R.E.E. in the calcite associated with the mineralisation indicates that the dolostones were not formed as an early phase of the lead-zinc mineralisation. However, it is difficult to distinguish between the other modes of origin, due to insufficient information concerning the behaviour of R.E.E. in these environments. Certainly, it would appear that hypersaline brines could give the R.E.E. distribution found in the Wirksworth dolostones, whereas a possible origin in mixed waters or connate brines cannot be discussed fully without further information.

It must not be concluded that the writer is advocating that the Wirksworth dolostones have a connate brine origin because, as seen in Section 7.3.2(b), there is a great deal of variability in the published literature for these brines, indeed the conditions existing in any of the environments appear very variable and explain the great uncertainty which surrounds not only the origin of the Wirksworth dolostones but of many others.

C H A P T E R E I G H T

8. CONCLUSIONS

The Lower Carboniferous rocks of the Wirksworth area, Derbyshire, consist essentially of massively-bedded limestones and dolostones. The original carbonate sediments were of Asbian and Brigantian age, comprising the Hoptonwood and Matlock Groups, with isolated outcrops of the uppermost Cawdor Group. These sediments have been affected by the following stages of diagenesis and alteration (figure 52):

1) Early marine and later meteoric diagenesis prior to the end of the Lower Carboniferous caused the induration of these carbonate sediments. Algal micritisation, primary and secondary cementation, pressure solution and aggrading neomorphism played a significant part in this induration. The bulk of the diagenesis occurred within the active phreatic zone, during one of the many periods of subaerial exposure during the Lower Carboniferous. The primary, very high porosity of the unconsolidated carbonate sediments became occluded during this Lower Carboniferous diagenesis to give the characteristic porosity (2 - 8 percent) of the limestones.

2) Pre-Namurian exposure caused the widespread karstification of the Lower Carboniferous Limestone. It has been estimated (Ford 1964) that a relief of approximately

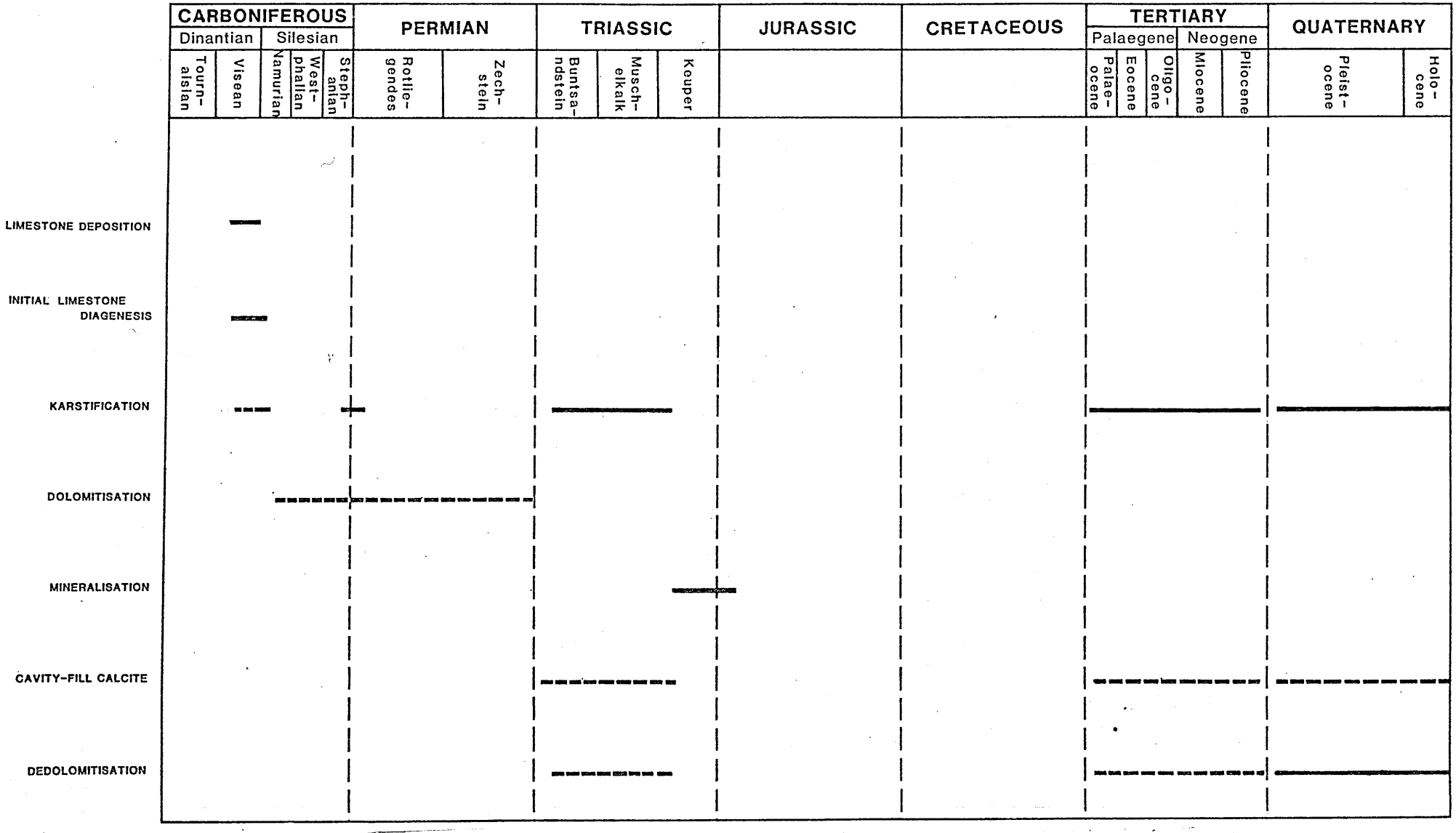


Figure 52 A summary of the diagenesis of the carbonate succession in the Wirksworth and surrounding areas, Derbyshire.

500 ft. was developed upon the limestone during this period. This relief and karstification played a significant role during dolomitisation, providing a ready access for the infiltrating dolomitising fluids.

3) Dolomitisation occurred prior to the late Triassic mineralisation and appears to have been controlled largely by the jointing of the former limestone. The dolostones consist mainly of xenotopic - hypidiotopic types showing many calcite filled polyhedral pores, although less common xenotopic and idiotopic types do occur. The completely dolomitised xenotopic dolostones are thought to represent former micarenites, whilst the less dolomitised xenotopic - hypidiotopic and idiotopic dolostones represent dolomitised crinoidal biomicarenites and biosparenites. It is felt that the less completely dolomitised limestones are a consequence of the abundance of crinoidal fragments, which often show good development of syntaxial rim and cavity-fill cements. However, where the access of the dolomitising fluids is exceptionally good, then even the crinoidal-rich limestones become totally dolomitised.

The polyhedral pores represent the incomplete dolomitisation of sparry material, occurring mainly as crinoidal fragments, although coarse cavity-fill cements are also important. The remnant calcite filling in these pores became leached either during or after dolomitisation to give quite high primary porosity to the dolostones.

The varying degrees of dolomitisation gave rise to a number of porosities, from the low porosities of the xenotopic dolostone, indicating a volume for volume replacement, to the higher porosity of the less completely dolomitised idiotopic dolostones. These variable primary porosities became occluded during a later meteoric phase by a cavity-fill cement.

A study of the major and trace element geochemistry of the dolostone gave no conclusive evidence concerning the origin of the dolomitising fluids. Most of the elemental concentrations found in these dolostones can be accounted for in any of the environments proposed for the formation of the dolomite, ie. hypersaline, groundwater (mixed water and connate) or hydrothermal. It is the sodium and strontium concentrations which prove most useful. The fairly high Na^{+} and low Sr^{2+} concentrations do not support a hypersaline or mixed water (brackish) origin. These concentrations can be more fully accounted for if a connate water origin is considered, although again the sodium values do appear a little high. A comparison of the dolostone and the gangue calcite of the mineralisation indicated that the dolomitisation was unlikely to have been associated with the hydrothermal fluids. The rare earth element geochemistry shows that the dolomitising fluids did not have a similar origin to the mineralising fluids due to the greater concentrations of the R.E.E. shown by the gangue calcite. However, the other types

of dolomitising fluids cannot be distinguished between using this method. The calcite of the mineralisation shows an enrichment of rare earth elements, which is not present in the dolostones. The evolution of the rare earth elements trapped within sediments at depth has not been studied and thus no direct evidence for or against a connate brine origin can be presented.

4) After this period of dolomitisation the undulating base of the dolostone became karstified to give an extensive cave system due to the exposure of the Lower Carboniferous Limestone during the Triassic, prior to the infilling of these caves by lead-zinc mineralisation in the late Triassic.

5) Sub-aerial weathering during the Triassic, pre-Pleistocene and predominantly post-Pleistocene has allowed dedolomitisation and leaching to occur. This has allowed the regeneration and enhancement of the primary porosity of the dolostones.

Dedolomitisation occurs mainly around the calcite-filled polyhedral pores and is thought to be largely a consequence of vadose rather than phreatic conditions because of (a) the enhanced porosities found associated with the dolostone tors; (b) it's widespread occurrence just below the soil horizon; (c) it's presence above clay wayboards and finally (d) the presence of high magnesium calcite, which is often marked by pores due to it's greater

solubility. It is felt that phreatic waters, which are often charged with excess calcium sulphate, would cause a more pervasive dedolomitisation, similar to that found in the Jura Mountains by Evamy (1967). The dedolomitisation process can be shown to have many stages of alteration ranging from slight corrosion around dolomite euhedra to complete dolomitisation. Complete dedolomitisation is rare and is only associated with the dolomitic limestones and mineralisation.

Dedolomitisation has been found to be very localised and is associated with the karst features, such as solution-widened bedding, jointing and fracturing. These allow the required access for aggressive waters to penetrate along the dolomite - calcite interface of the calcite-filled pores. These waters become saturated with Ca^{2+} and thus cause dedolomitisation. Away from these features only a limited alteration has occurred.

A rather distinct type of dedolomitisation has been found in these dolostones, i.e. the dedolomitisation of the large crinoidal dolomite pseudomorphs. The pseudomorphs are commonly degraded to dolomicrite and consequently, in the presence of Ca^{2+}-rich waters, became dedolomitised. The resulting calcite becomes leached to give mouldic vugs, often showing a remnant rim of optically continuous dolomite which represents the dolomitised syntaxial rim.

Leaching has caused the development of localised high

porosity in the dolostones, next to solution-widened bedding, jointing and fracturing, due to the removal of pore-filling and dedolomitisation calcites. The extent of leaching in these regions is heavily dependent upon the original fabric of the dolostone and the degree of dedolomitisation. For example, adjacent to these channels an incompletely dolomitised idiotopic dolostone may become extensively dedolomitised (due to the presence of excess Ca^{2+}) which, upon leaching, will give a very good porosity. If alteration continues then the dolostone may collapse and cause widening of the channel. A more completely dolomitised xenotopic - hypidiotopic dolostone in this situation would also develop high porosity but normally would not become as altered as the more Ca^{2+}-rich idiotopic dolostone. Completely dolomitised xenotopic dolostone usually remains quite resistant to dedolomitisation and leaching, even when occurring very close to these karst features.

Away from the channels leaching and dedolomitisation are limited and lower porosity develops. However, the presence of dolomite pseudomorphs, with their enhanced susceptibility towards dedolomitisation and leaching, may give rise to higher porosity, both here and in areas of excess leaching, next to channels.

One of the aims of this research was to establish whether or not predictions could be made concerning the occurrence of porosity in a dolostone formation weathering

under sub-aerial conditions. It is concluded that such predictions are virtually impossible due to: the localised nature of the leaching and dedolomitisation; the dependence of leaching and dedolomitisation upon dolostone fabrics; and the vagaries of the karstification process. The variability of the dolostone fabrics has been found to be a consequence of the fabric variation of the original limestone, and the access given to the dolomitising fluids. The unpredictability of the karstification is due to it's dependence upon many variables, such as climate, relief, tectonics and time.

Any future research concerning the development of porosity in dolostone formations, weathering under sub-aerial conditions must include:-

(a) an investigation of the effect which climate, vegetation, relief and tectonics may have upon the karst-related dolostone porosity.

(b) a detailed investigation of the influence particular limestone fabrics have upon the formation of the different types of dolostone; and

(c) an investigation of the trace element geochemistry of the dolostones and of the waters thought to induce dolomitisation. In particular, it may be found that an investigation of the rare earth element distributions may prove fruitful, together with an investigation of strontium and niodinium isotopes.

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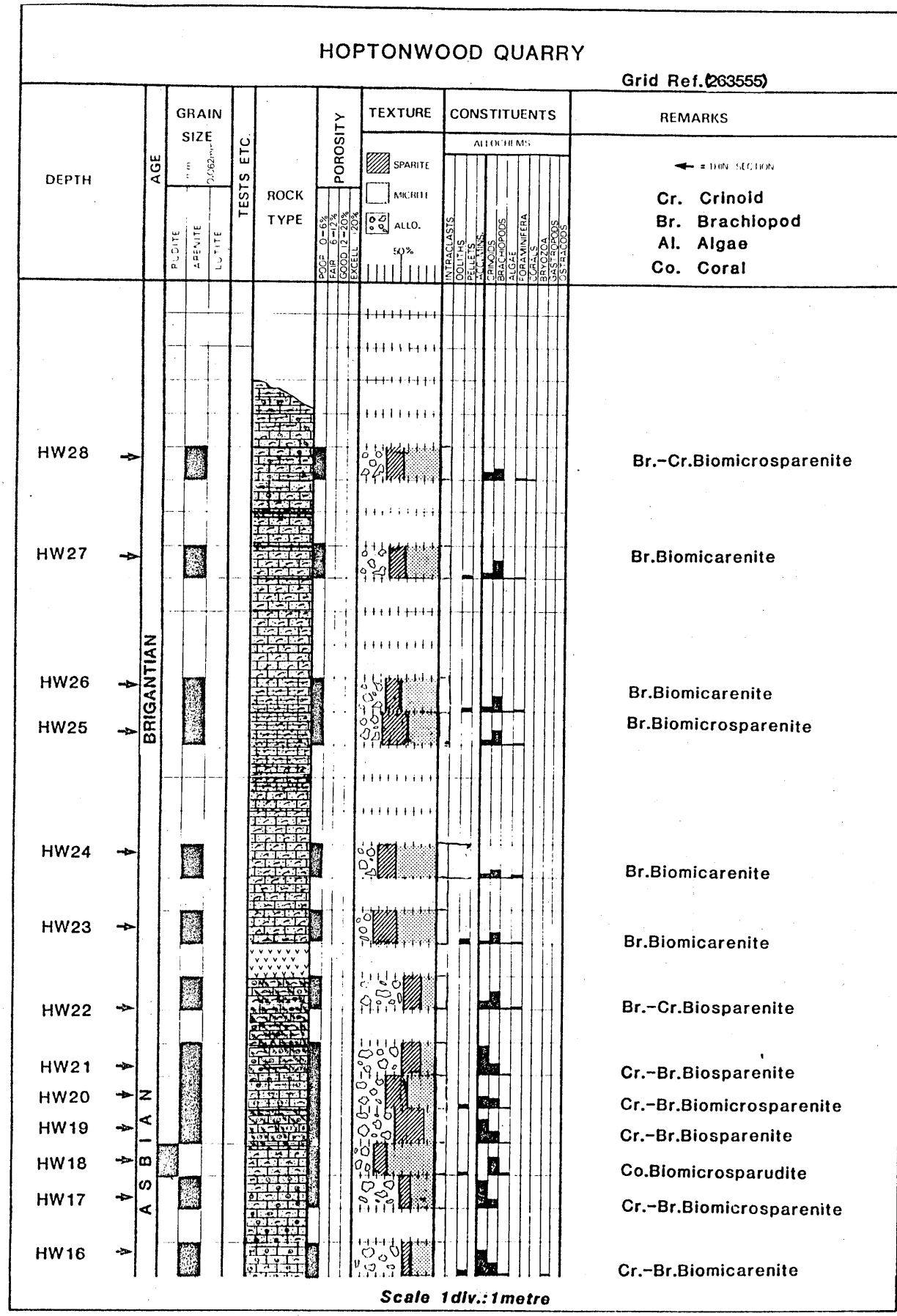
A P P E N D I X I


HOPTONWOOD QUARRY
Grid Ref.(263555)
DEPTH
AGE
GRAIN SIZE
TESTS ETC.
ROCK TYPE
POROSITY
TEXTURE
CONSTITUENTS
REMARKS
SPARITE
MICRITE
ALLO.
50%
ALLOCHEMS
INTRACLASTS
OOLITHS
PELLETS
CRINOIDS
BRACHIOPODS
ALGAE
FORAMINIFERA
CORALS
BRYOZOA
GASTROPODS
OSTRACODS
= THIN SECTION
Cr. Crinoid
Br. Brachiopod
Al. Algae
Co. Coral
BRIGANTIAN
ASBIAN
HW28
HW27
HW26
HW25
HW24
HW23
HW22
HW21
HW20
HW19
HW18
HW17
HW16
Br.-Cr.Biomicrosparenite
Br.Biomicarenite
Br.Biomicarenite
Br.Biomicrosparenite
Br.Biomicarenite
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Cr.-Br.Biomicrosparenite
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Scale 1div.:1metre

HOPTONWOOD QUARRY(contd.)

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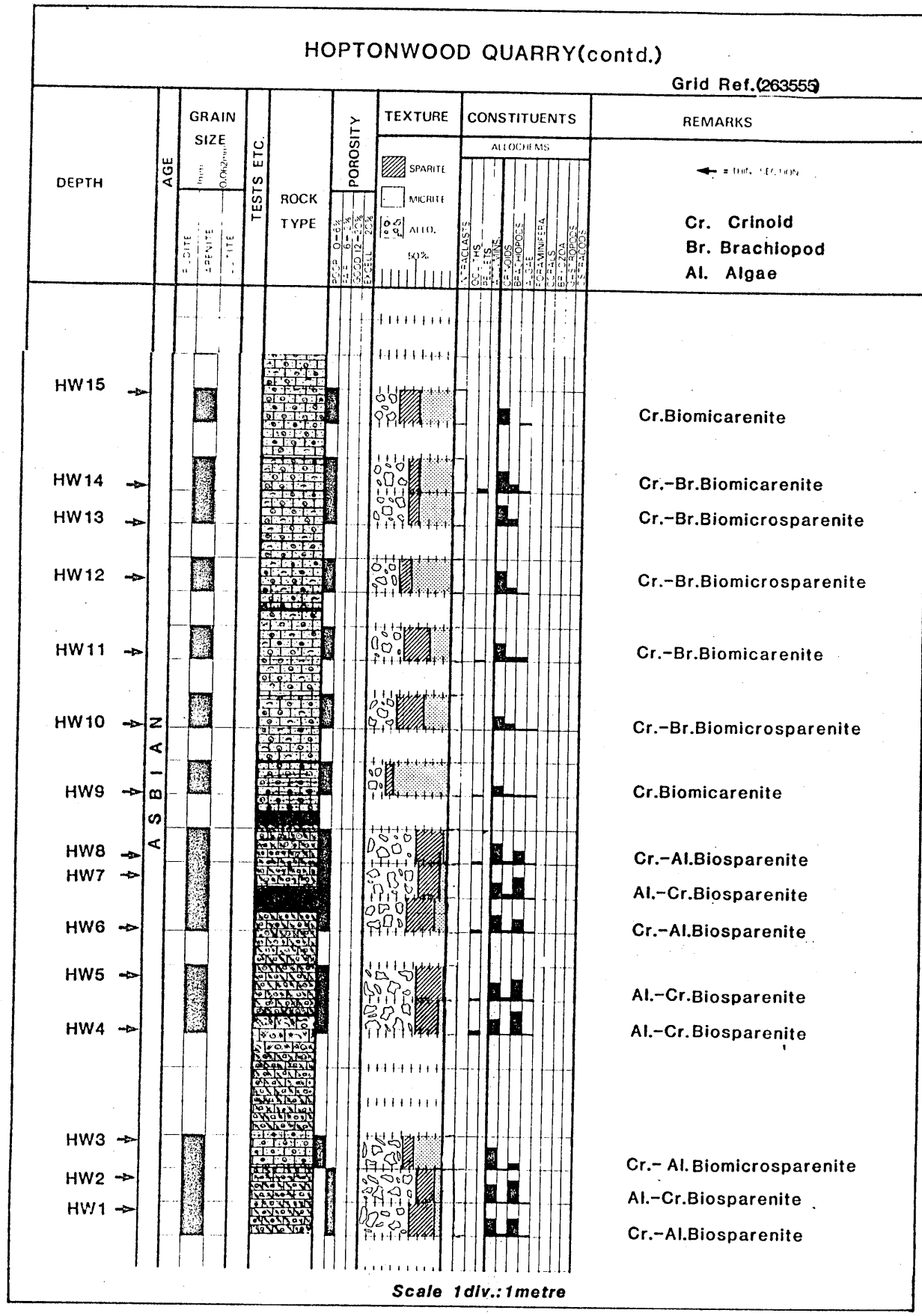

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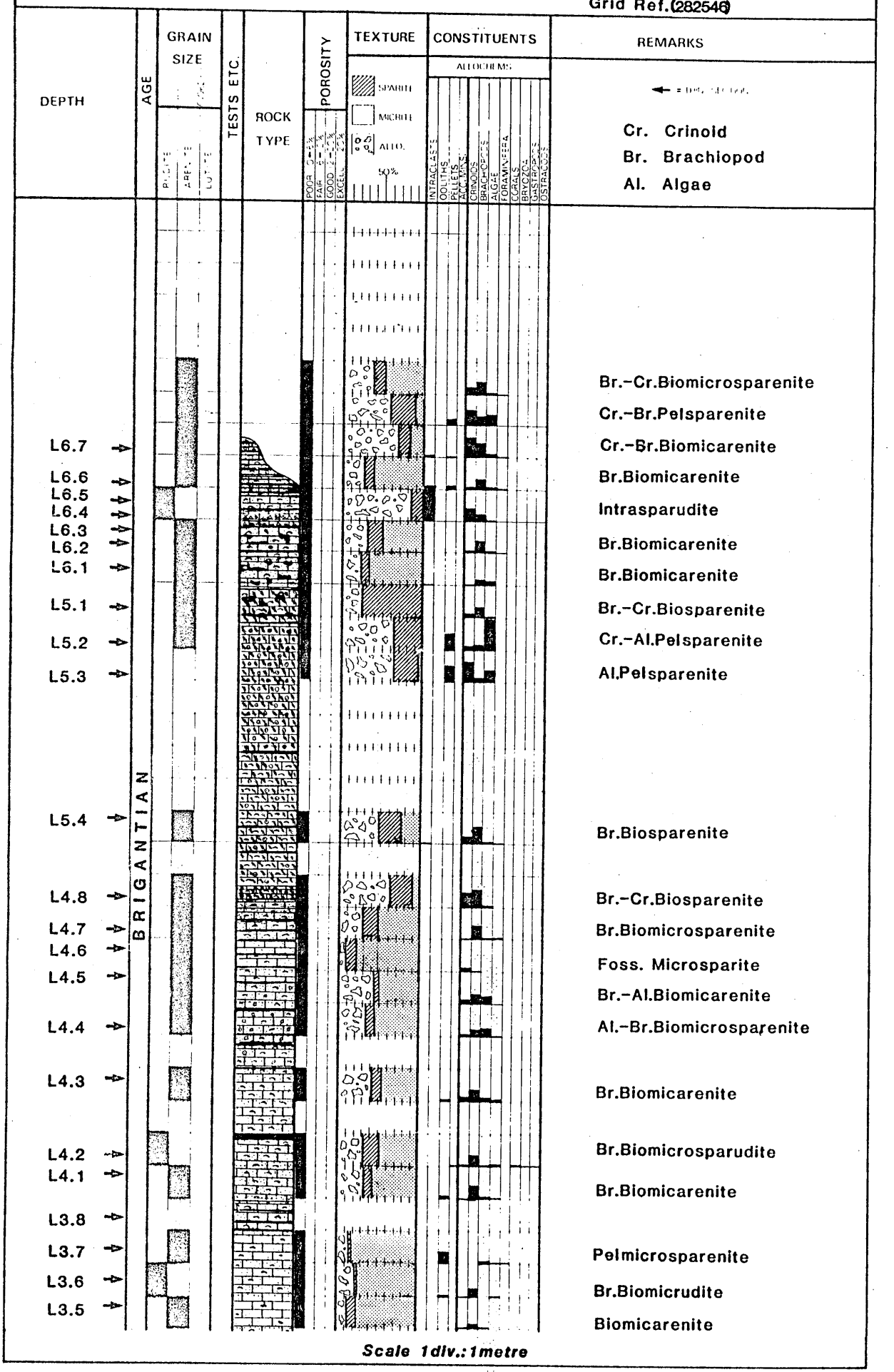

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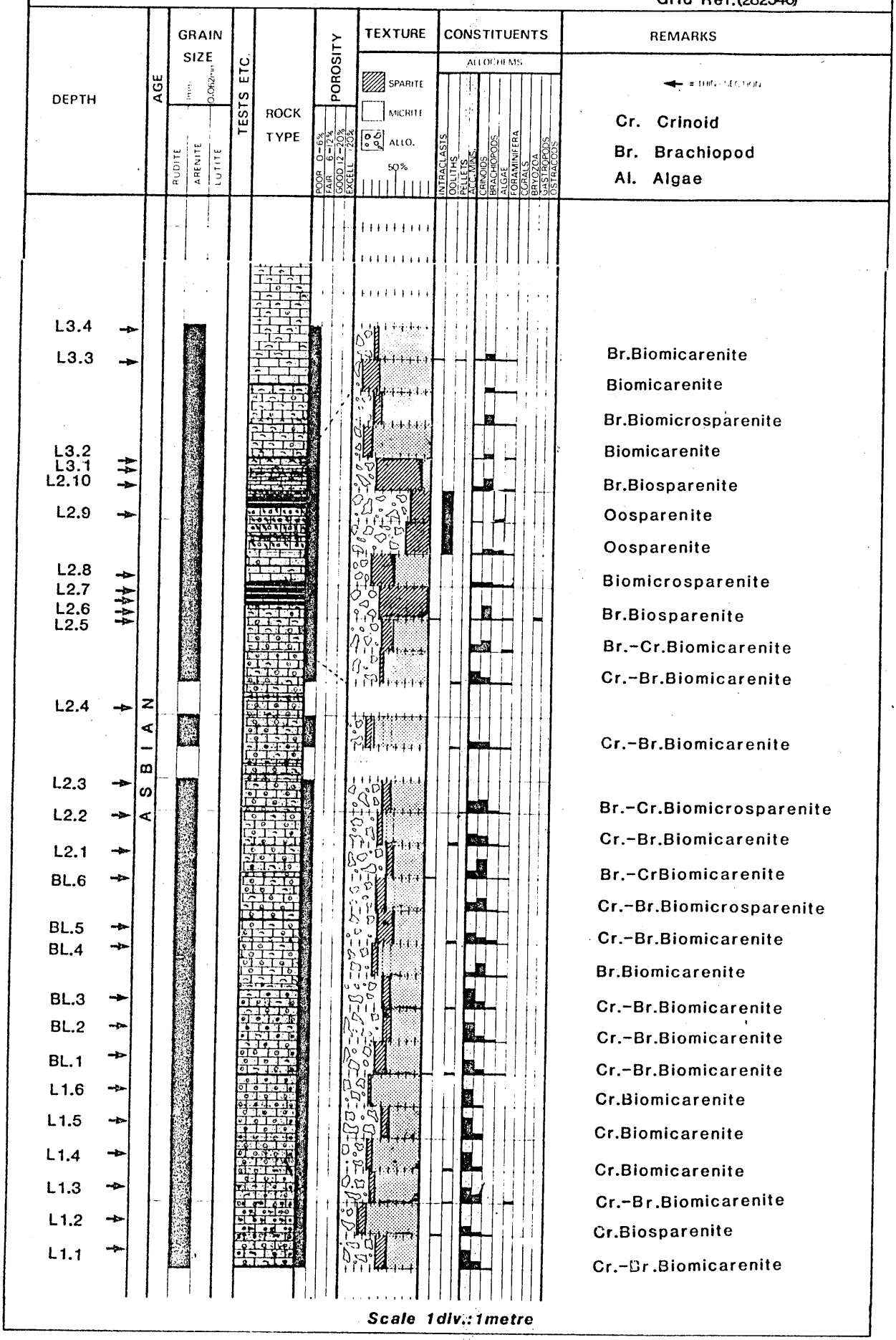

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INTAKE QUARRY

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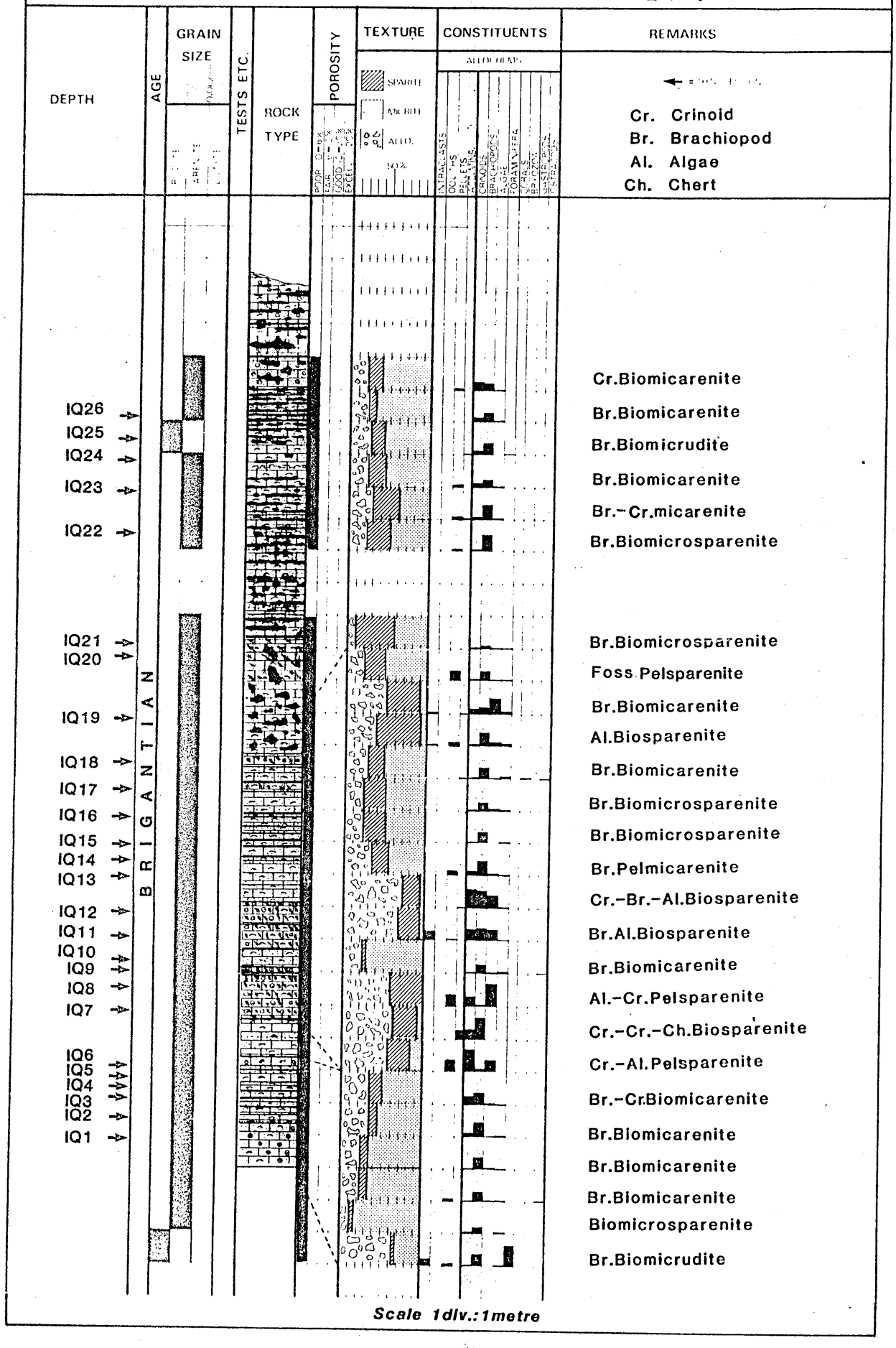


A P P E N D I X I I

A P P E N D I X I I I

Probe Analysis

Probe analyses shown in Tables IV and VI were performed at the Open University using the Department's fully computerised Cambridge Mk 9 Microprobe. Samples consist of highly polished rock thin sections. The basic conditions used for silica analysis i.e. a filament voltage of 20KeV and a probe current of 60nA were found to decompose the carbonates and therefore invalidate the analysis. Thus, new conditions of analysis were found for these carbonates.

Conditions of Analysis

It was found that a probe current of 3nA, a similar KeV to that above and a defocused beam prevented any decomposition occurring during the analysis. The lower probe current demanded much longer count times, to accumulate the necessary counts (50,000 cts.). The count times used were 100 seconds for Mg and Ca and 200 seconds for Fe and Mn. This gave an overall analysis time of approximately 15 minutes. These long analysis times require the constant monitoring of the sample current and elemental counts on a chart recorder to detect any decomposition. It was found that using these conditions, detection limits of approximately 0.05% for each element might be expected. Only Mg, Ca, Fe and Mn were found in quantities greater than these detection limits.

Elemental counts per second of the unknowns are compared directly to counts per second of standards for each element, which are of known composition. The standards used during these analyses were:-

Standard:	Element:
Synthetic MgO (Open Univ.)	Magnesium
Wollastonite (Brit. Mus.)	Calcium
Fayalite	Iron
Manganese Metal	Manganese

Internal standards used were:-

Iceland Spar

Vein Dolomite

The Technique

Highly polished rock thin sections are bombarded with electrons in the sample chamber of the probe. Using a defocussed beam as in this study, an area of approximately 20μm. in diameter is activated. The emitted x-rays are dispersed through a high precision crystal and then each x-ray is counted at characteristic angles. These angles, which are dependent upon the wavelength of the x-rays, are characteristic of each element. The x-rays are counted using flow counters carried by movable spectrometers. The corrected counts are directly compared to standards of known composition to give the elemental concentrations.

A P P E N D I X I V

Porosity Determination

As noted in Chapter V, porosity determinations were made using core and chip samples. The drill chips came mainly from the Ryder Point Borehole (Section 5.3.5) and consist of 0.5 - 1.0 cms. sized chips. These presented particular problems during analysis.

Core Samples

The porosity of the cores was determined using a simple wet-dry method, which was found to give good results.

1) the cores are cleaned in deionised water and then dried in an oven overnight.
2) their volumes are measured using graduated calipers.
3) the cores are weighed dry.
4) the cores are immersed in deionised water for at least one week, whereupon an adequate saturation was found to have occurred.
5) the cores are weighed whilst saturated.

The porosity is simply determined using the following expression:-

$$\text{Porosity} = 100 \times \frac{\text{Volume of voids}}{\text{Volume of sample}}$$

$$= 100 \times \frac{\text{Sat. Wt. - Dry Wt.}}{\text{Volume of sample}}$$

To determine the accuracy of the method two standards were analysed. A non-porous metallic cube, which gave a

result of 0.4%, and a Bunter Sandstone core of known porosity (21.5% J. Finch, Univ. Birm.), which gave a result of 20.9%.

Chip Samples

A similar wet-dry method to that described above was used to determine the porosity of the chips.

1) the chips are thoroughly cleaned in deionised water to remove any excess drilling mud.

2) the chips are dried in an oven overnight and then weighed.

3) to determine their volume the chips are placed in a 50 ml. volumetric flask and immersed in deionised water. The chips are left for one week (until saturated) and the flask filled and weighed. The bulk volume of the chips ie. the total volume-volume of voids will equal:

$$\text{Wt. of vol. flask + water} = \text{Wt. of vol. flask + water + chips} - \text{Wt. of chips}$$

$$\text{Porosity \%} = 100 \times \frac{\text{Vol. of voids}}{\text{Vol. of sample}}$$

$$\text{Vol. of voids} = \text{Sat. Wt.} - \text{Dry Wt.}$$

$$\text{Vol. of sample} = \text{Bulk vol.} + \text{Vol. of voids}$$

The accuracy of this method was gauged by analysing samples as cores and chips. The comparison of the results from these two methods is shown below:-

Comparison of chip and core techniques

Sample	Core results	Chip results
$B_2 7$	6.80	8.35
$B_2 11$	5.86	7.38
$B_2 15$	7.73	6.38
$B_2 16$	10.38	11.45
$B_2 24$	4.30	4.65

TRAVERSES (core samples)

SAMPLE NO.	POROSITY %	SAMPLE NO.	POROSITY %
1A	1.30	7A	2.13
1B	1.54	7B	4.17
1C	2.47	7C	13.68
1D	0.96	7D	12.38
2A	0.99	8A	1.47
2B	2.30	8B	3.33
2C	4.17	8C	8.24
3A	1.39	8D	3.26
3B	0.99	8E	5.41
3C	8.16	8F	2.52
4A	0.97	8G	11.82
4B	1.12	8H	6.25
4C	10.20	8L	11.34
5A	1.19	9A	8.16
5B	2.75	9B	8.75
6A	9.01	9C	3.26
6B	11.38	10A	22.52
6C	2.44	10C	15.69
6D	4.65	10D	3.88
6E	4.42	10E	17.3
6F	2.08	10F	8.26

NEW HARBOROUGH FARM
BOREHOLE (core samples)

SAMPLE NO.	POROSITY %
B_2P1	8.00
B_2P2	6.96
B_2P3	8.88
B_2P4	9.45
B_2P5	10.50
B_2P6	6.65
B_2P7	6.97
B_2P8	10.00
B_2P9	3.30
B_2P10	7.59
B_2P11	5.48
B_2P12	2.30
B_2P13	6.11
B_2P13A	7.09
B_2P14	8.38
B_2P15	7.73
B_2P16	7.89
B_2P17	2.14
B_2P18	7.20
B_2P19	13.40
B_2P20	16.70
B_2P21	8.17
B_2P22	4.56
B_2P23	1.85
B_2P24	2.84

LIMESTONE SAMPLES (cores)

SAMPLE NO.	POROSITY %
$L_1 6$	4.76
$L_2 7$	1.54
$L_2 10$	5.45
$L_4 5$	2.60
$L_6 2$	1.75
$L_6 6$	1.85
$L_7 6$	2.70
IQ7	5.77
IQ16	5.45
IQ20	3.77
HW1	10.8
HW8	7.69
HW18	5.00
HW26	2.41

HARBOROUGH ROCKS SECTION
(core samples)

SAMPLE NO.	POROSITY %
HR1	26.56
HR2	41.03
HR3	31.33
HR4	32.03
HR5	38.60
HR6	30.19
HR7	54.40
HR8	36.39
HR9	30.54
HR10	49.28
HR11	43.84

MONYASH BOREHOLE
(core samples)

SAMPLE NO.	POROSITY %
2.15	4.60
3.92	2.87
4.79-5.66	6.15
5.66	2.22
6.52(1)	3.32
6.52(2)	8.89
7.39	2.46
9.05-9.85	4.21
10.00	22.63
17.56	15.69
20.05	16.26
28.50	12.78
29.85	17.81
30.75	17.20
31.69	8.14
32.85	17.47
35.25	9.18
40.36	14.81
40.72	11.29
42.54	11.54
46.10	5.25

RYDER POINT BOREHOLE (chip samples)

SAMPLE NO.	POROSITY %	SAMPLE NO.	POROSITY %	SAMPLE NO.	POROSITY %
3-6	15.2	61-64	17.9	118-121	18.7
6-9	24.2	64-67	7.8	121-124	8.6
9-12	20.2	67-70	20.2	124-127	12.9
12-15	20.8	70-73	17.7	127-130	12.0
15-18	24.2	73-76	23.7	130-133	11.1
18-21	22.7	76-79	15.6	133-136	11.5
21-24	17.3	79-82	8.8	136-139	12.4
24-27	23.8	82-85	13.7	139-142	9.0
27-30	25.0	85-88	17.7	142-145	9.4
30-33	26.8	88-91	10.9	145-148	8.7
33-36	17.6	91-94	10.0	148-151	13.1
36-39	22.2	94-97	12.7	151-154	10.5
39-42	10.5	97-100	8.5	154-157	6.4
42-45	14.7	100-103	9.8	157-160	8.0
45-48	8.2	103-106	13.8	160-163	5.9
48-51	6.9	106-109	12.1	163-166	12.1
51-54	10.9	109.112	21.1	166-169	7.8
55-58	13.6	112-115	11.5	169-172	7.4
58-61	4.9	115-118	14.3		

HARBORO' BOREHOLE No. 1.

Footage	CaO %	MgO %	Porosity %
3' - 5'	30.6	21.4	20.0
5' - 7'	31.8	20.4	18.3
7' - 9'	30.4	21.6	16.5
9' - 11'	31.2	21.0	18.3
11' - 13'	31.4	20.8	19.4
13' - 15'	31.4	20.7	20.8
15' - 17'	32.0	20.2	16.9
17' - 19'	31.8	20.4	19.8
19' - 21'	31.8	20.4	18.7
21' - 23'	31.6	20.6	15.9
23' - 25'	31.8	20.3	14.4
25' - 27'	31.6	20.5	16.2
27' - 29'	32.4	19.9	16.2
29' - 31'	33.2	19.2	15.5
31' - 33'	32.6	19.7	15.9
33' - 35'	32.6	19.7	18.3
35' - 37'	31.6	20.4	16.2
37' - 39'	32.2	20.0	16.2
39' - 41'	32.6	19.3	20.0
41' - 43'	32.2	19.6	14.8
43' - 45'	31.8	20.2	18.3
45' - 47'	31.0	20.2	16.2
47' - 49'	30.6	20.8	16.5
49' - 51'	31.6	20.3	17.6
51' - 53'	31.6	20.4	15.2
53' - 55'	32.0	20.3	15.2
55' - 57'	32.0	20.3	16.5
57' - 59'	31.8	20.4	17.6
59' - 61'	31.0	20.2	17.6
61' - 63'	31.6	20.2	16.5
63' - 65'	33.0	19.3	17.6
65' - 67'	32.6	19.5	19.0
67' - 69' (67'9 - 68'3 shale)	33.2	19.0	15.2
69' - 71'	32.4	20.0	14.4
71' - 73'	32.4	19.6	15.9
73' - 75'	31.8	20.4	15.9
75' - 77'	32.4	19.9	15.2
77' - 79'	32.2	20.0	14.4
79' - 81'	31.6	20.6	13.0
81' - 83'	32.6	19.4	12.0
83' - 85'	31.4	20.3	14.1
85' - 87'	32.0	19.7	15.2
87' - 89'	32.2	19.7	13.8
89' - 91'	32.0	19.8	14.4
91' - 93'	33.0	19.0	13.0
93' - 95'	31.6	20.4	13.4
95' - 97'	32.0	20.2	15.2
97' - 99'	32.0	20.3	15.2
99' - 101'	32.0	20.1	14.4
101' - 103' (101'3"-101'6" clay)	28.8	18.0	16.5
103' - 105'	31.4	20.6	16.2
105' - 107'	31.8	20.4	16.5
107' - 109'	31.8	20.4	15.5
109' - 111'	32.8	19.6	15.2
111' - 113'	32.4	19.7	15.9
113' - 115'	31.6	20.6	17.2
115' - 117'	31.8	20.5	17.2
117' - 119'	32.2	20.2	18.3
119' - 121'	31.8	20.4	17.2
121' - 123'	32.2	20.2	16.9
123' - 125'	31.6	20.6	17.6
125' - 127'	31.8	20.6	16.2
127' - 129'	32.2	20.1	16.5
129' - 131'	32.4	19.8	15.5
131' - 133'	32.8	19.6	18.0
133' - 135'	32.4	20.0	20.5
135' - 137'	33.4	19.2	18.0
137' - 139'	33.0	19.4	19.8
139' - 141'	32.0	20.0	16.9
141' - 143'	32.2	20.0	15.9
143' - 145'	32.0	20.2	15.5
145' - 147'	32.8	19.6	13.8
147' - 149'	32.4	19.9	16.2
149' - 151'	32.8	19.4	16.2
151' - 153'	32.4	20.0	11.7

HARBORO' BOREHOLE No. 2.

Footage	CaO %	MgO %	Porosity %
1' - 3'	32.8	19.5	17.6
3' - 5'	32.4	20.0	20.0
5' - 7'	31.8	20.5	19.8
7' - 9'	31.4	20.8	20.8
9' - 11'	33.2	19.2	20.0
11' - 13'	32.4	19.6	16.2
13' - 15'	33.4	19.0	18.0
15' - 17'	34.0	18.4	16.2
17' - 19'	33.4	18.9	17.2
19' - 21'	32.8	19.3	18.3
(20' - 20'2" clay)			
21' - 23'	31.2	17.9	18.3
23' - 25'	33.2	19.1	18.0
25' - 27'	32.0	20.3	19.0
27' - 29'	32.4	19.9	18.3
29' - 31'	31.6	20.6	19.0
31' - 33'	31.4	20.8	18.7
33' - 35'	32.2	20.0	18.7
35' - 37'	32.6	19.6	17.2
37' - 39'	34.0	18.4	14.4
39' - 41'	34.6	18.0	12.3
41' - 43'	33.0	19.3	13.0
43' - 45'	33.2	19.2	13.0
45' - 47'	32.8	19.5	13.8
47' - 49'	32.4	19.8	13.0
49' - 51'	32.6	19.6	14.1
51' - 52'7"	32.0	20.1	14.4
52'7" - 54'	32.0	19.3	8.1
(54' - 55'6" shale)			
56'6" - 58'	32.6	19.6	16.2
58' - 60'	32.6	19.7	15.2
60' - 62'	32.0	20.3	15.5
62' - 64'	32.4	20.0	14.7
64' - 66'	33.0	19.4	15.8
66' - 68'	35.6	17.2	15.8
68' - 69'	34.2	17.8	14.4
(69' - 71' clay)			
71' - 73'	32.2	18.8	17.3
73' - 75'	33.6	18.7	21.8
75' - 77'	32.0	20.2	22.1
77' - 79'	31.2	20.8	21.5
79' - 81'	31.6	20.6	20.4
81' - 83'	31.2	21.0	20.0
83' - 85'	31.8	20.4	18.3
85' - 87'	31.6	20.4	19.0
87' - 89'	32.4	19.9	16.2
89' - 91'	32.0	20.0	17.7
91' - 93'	32.4	19.8	16.9
93' - 95'	32.6	19.8	20.4
95' - 97'	32.8	19.7	19.0
97' - 99'	32.0	20.3	19.4
99' - 101'	32.4	20.0	18.0
101' - 103'	32.4	20.0	20.4
103' - 105'	31.8	20.5	20.0
105' - 107'	32.6	19.8	19.4
107' - 109'	31.8	20.5	20.0
109' - 111'	32.2	20.2	20.4
111' - 113'	32.2	20.2	20.4
113' - 115'	32.8	19.5	16.2
115' - 117'	32.6	19.8	14.8
117' - 119'	32.4	19.8	13.8
119' - 122'4"	33.6	18.8	14.4
(122' - 124'3" shale)			
125' - 127'	33.2	18.6	11.2
127' - 129'	32.6	19.0	13.0
129' - 131'	32.6	19.4	16.2
131' - 132'3"	33.2	19.4	13.4

HARBORO' BOREHOLE No. 3.

Footage	CaO %	MgO %	Porosity %
0'-16'6"	31.6	20.3	
16'6"-18'	32.0	20.0	21.9
18' - 20'	32.0	20.0	20.0
20' - 22'	31.8	20.1	22.6
22' - 24'	31.6	20.6	21.1
24' - 26'	32.0	19.9	22.1
26' - 28'	31.7	20.2	15.5
28' - 30'	31.6	20.2	12.3
30' - 32'	31.4	20.6	12.0
32' - 34'	32.0	20.2	10.9
34' - 36'	32.0	20.2	10.2
36' - 38'	32.0	20.1	15.2
38' - 40'	32.0	20.3	15.2
40' - 42'	32.2	20.0	16.2
42' - 44'	32.6	19.6	14.4
44' - 46'	32.6	19.6	16.2
46' - 48'	31.8	20.4	14.0
48' - 50'	32.2	19.8	15.5
50' - 52'	32.6	19.0	15.5
52' - 54'	33.2	19.0	16.2
54' - 56'	34.6	18.1	15.8
56' - 58'	32.0	20.2	17.7
58' - 60'	32.8	19.6	16.9
60' - 62'	32.8	19.7	16.6
62' - 64'	32.6	19.6	14.3
64' - 66'	32.0	20.3	14.6
66' - 68'	32.2	20.2	16.2
68' - 70'	33.2	19.3	15.9
70' - 72'	32.6	19.6	20.0
72' - 74'	31.4	19.0	15.8
74' - 75'6"	32.2	19.2	16.6
75'6" - 76'3"			
76'3" - 79'	34.0	18.1	15.5
79' - 81'	35.8	16.7	16.6
81' - 83'	32.4	20.0	17.2
83' - 85'	32.6	19.8	17.7
85' - 87'	32.2	20.2	18.2
87' - 89'	32.2	20.2	18.2
89' - 91'	32.6	19.8	17.7
91' - 93'	33.0	19.4	15.8
93' - 95'	32.2	20.1	19.4
95' - 97'	33.2	19.1	18.0
97' - 99'	34.6	17.9	15.2
99' - 101'	32.6	19.7	21.1
101' - 103'	32.4	20.0	22.4
103' - 105'	32.4	20.1	16.5
105' - 107'	33.8	18.8	15.5
107' - 109'	32.8	19.7	19.4
109' - 111'	32.6	19.8	16.5
111' - 113'	33.2	19.2	18.3
113' - 115'	31.8	20.6	20.8
115' - 117'	32.4	20.2	16.2
117' - 119'	33.2	19.4	16.2
119' - 121'	34.2	18.5	21.1
121' - 123'	34.0	18.7	22.8
123' - 125'	33.2	19.5	19.0
125' - 127'	32.0	20.1	19.0
127' - 129'	32.6	19.9	19.8
129' - 131'	31.8	20.9	19.8
131' - 133'	31.6	20.8	19.8
133' - 135'	31.4	20.8	20.4
135' - 137'	31.4	20.8	20.0
137' - 139'	31.6	20.7	19.4
139' - 141'	32.8	19.7	13.8
141' - 143'	33.4	18.9	18.3
143' - 145'	32.0	20.2	19.8
145' - 147'	30.8	21.1	20.4
147' - 149'	31.4	20.7	28.5
149' - 151'	31.6	20.7	18.3
151' - 153'	31.8	20.5	20.8
153' - 155'	31.2	20.6	18.3

HARBORO' BOREHOLE No. 4.

Footage	CaO %	MgO %	Porosity %
Overburden 1'6"			
1'6" - 3'6"	31.2	20.9	15.5
3'6" - 5'6"	31.8	20.4	16.2
5'6" - 7'6"	31.6	20.5	16.9
7'6" - 10'6"	31.0	20.6	
10'6" - 12'6"	31.4	20.7	15.5
12'6" - 14'6"	31.4	20.7	18.7
14'6" - 16'6"	31.6	20.6	17.9
16'6" - 18'6"	31.2	20.8	17.9
18'6" - 22'0"	31.2	20.7	San
22' - 24'	34.6	17.8	18.2
24' - 26'	33.8	18.7	13.1
26' - 28'	34.6	17.9	19.0
28' - 30'	35.2	17.3	19.7
30' - 32'	33.2	19.1	17.2
32' - 34'	32.6	19.7	22.5
34' - 36'	32.4	19.7	23.9
36' - 38'	32.2	20.0	25.0
38' - 40'	32.6	19.6	22.5
40' - 42'	33.2	19.2	22.5
42' - 44'	33.4	19.1	21.5
44' - 46'	33.0	19.4	22.5
46' - 48'	32.8	19.5	21.1
48' - 50'	33.4	18.8	21.1
50' - 52'	32.8	19.6	20.0
52' - 54'	32.8	19.5	17.9
54' - 56'	32.0	20.0	17.6
56' - 58'	31.6	20.5	16.6
58' - 60'	32.0	20.2	15.1
60' - 62'	31.8	20.4	15.8
62' - 64'	32.2	19.9	9.5
64' - 66'	32.2	19.8	13.0
66' - 68'	32.0	20.3	11.3
68' - 70'	32.4	19.7	14.4
70' - 72'	32.4	19.8	15.1
72' - 74'	31.6	20.5	18.2
74' - 76'	32.4	19.8	16.2
76' - 78'	31.6	20.4	20.4
78' - 80'	31.2	20.8	19.0
80' - 82'	32.6	19.7	17.2
82' - 84'	32.0	20.3	18.7
84' - 86'	31.4	20.6	19.7
86' - 88'	32.0	20.2	18.7
88' - 90'	33.4	19.0	19.0
90' - 92'	33.4	19.2	16.6
92' - 94'	31.2	20.7	21.9
94' - 96'	32.0	19.4	19.0
96' - 98'	31.4	20.7	22.1
98' - 100'	31.8	20.4	21.1
100' - 102'	31.2	20.9	20.8
102' - 104'	31.6	20.5	21.5
104' - 106'	31.6	20.5	23.3
106' - 108'	32.0	20.2	21.9
108' - 110'	30.6	20.7	22.5
110' - 112'	30.2	21.4	23.3
112' - 114'	30.6	21.6	24.7
114' - 116'	31.4	20.8	24.3
116' - 118'	31.4	20.8	21.1
118' - 120'	31.2	21.0	21.9
120' - 122'	30.4	21.7	21.9
122' - 124'	31.0	21.2	20.8
124' - 126'	30.8	21.3	22.5
126' - 128'	32.2	20.1	21.7
128' - 130'	32.0	20.3	19.0
130' - 132'	31.6	20.7	19.0
132' - 134'	31.6	20.7	19.7
134' - 136'	32.6	19.7	17.2
136' - 138'	33.2	19.2	17.9
138' - 139'	33.0	19.5	22.9
139' - 141'	32.8	19.5	17.2
141' - 143'	32.6	19.6	18.2
143' - 145'	32.2	20.1	21.9
145' - 147'	32.2	20.0	20.0
147' - 149'	32.4	20.0	18.2
149' - 151'	32.4	19.9	16.2
151' - 153'	31.8	20.4	17.6

HARBORO' BOREHOLE No. 5.

Footage	CaO %	MgO %	Porosity %
2' - 4'	31.0	21.2	27.1
4' - 6'	31.6	20.6	24.7
6' - 8'	31.6	20.7	26.1
8' - 10'	31.6	20.7	25.1
10' - 12'	31.6	20.7	23.6
12' - 14'	31.6	20.7	25.0
14' - 16'	32.4	20.0	21.1
16' - 18'	32.0	20.4	22.9
18' - 20'	32.6	19.9	20.5
20' - 22'	32.2	20.2	20.5
22' - 24'	32.8	19.5	18.2
24' - 26'	33.6	18.8	18.2
26' - 28'	33.6	18.8	16.9
28' - 30'	33.4	19.0	16.9
30' - 32'	32.4	19.9	20.5
32' - 34'	32.0	20.3	20.5
34' - 36'	31.8	20.4	15.3
36' - 38'	32.6	19.8	20.5
38' - 40'	32.8	19.6	20.5
40' - 42'	32.2	20.1	25.1
42' - 44'	32.4	19.9	21.5
44' - 46'	32.0	20.3	17.6
46' - 48'	32.4	19.8	16.9
48' - 50'	33.2	19.0	16.9
50' - 52'	33.0	19.4	16.9
52' - 54'	32.8	19.5	19.8
54' - 56'	32.4	20.0	19.8
56' - 58'	32.6	19.8	21.8
58' - 60'	32.0	20.3	22.9
60' - 62'	31.4	20.3	20.5
62' - 64'	31.2	20.8	21.1
64' - 66'	31.4	20.9	20.5
66' - 68'	31.4	20.8	21.1
68' - 70'	32.8	19.4	16.9
70' - 72'	33.2	19.1	17.6
72' - 74'	33.6	18.8	14.1
74' - 76'	32.8	19.4	15.5
76' - 78'	32.8	19.3	15.5
78' - 80'	32.0	20.2	16.9
80' - 82' (6" clay not incl.)	32.0	20.0	16.9
82' - 84'	32.8	19.4	19.8
84' - 86'	33.0	19.2	18.7
86' - 88'	32.6	19.7	20.0
88' - 90'	31.8	20.2	18.3
90' - 92'	32.0	20.2	19.0
92' - 94'	32.8	19.6	19.7
94' - 96'	32.8	19.4	16.5
96' - 98'	36.6	15.8	19.4
98' - 100'	32.2	20.0	17.6
100' - 102'	31.6	20.2	18.0
102' - 104'	31.6	20.3	17.6
104' - 106'	31.2	20.4	21.5
106' - 108'	30.0	18.0	16.2
108' - 110'	31.6	20.6	18.0
110' - 112'	30.8	19.0	13.4
112' - 114'	32.6	19.7	17.6
114' - 116'	31.8	20.3	19.0
116' - 118'	31.0	19.1	17.6
118' - 120'	33.0	18.1	16.2
120' - 122'	33.6	18.8	18.7
122' - 124'	32.2	20.2	19.4
124' - 126'	32.6	19.8	17.6
126' - 128'	33.0	19.6	13.4
128' - 130'	32.8	19.8	20.0
130' - 132'	32.4	20.0	21.1
132' - 134'	33.2	19.4	20.0
134' - 136'	32.0	20.3	19.7
136' - 138'	32.0	20.4	16.5
138' - 140'	31.8	20.6	16.9
140' - 142'	31.8	20.6	19.0
142' - 144'	32.8	19.6	16.2
144' - 146'	33.2	19.4	13.4
146' -148'8" (148'8" - 151'	33.0	19.2	16.2
151' - 153'	33.6	18.6	14.1
153' - 155'	31.2	21.0	17.6
155' - 157'	31.4	20.9	17.6
157' - 159'	31.6	20.7	19.4

HARBORO' BOREHOLE No. 6.

Footage	CaO %	MgO %	Porosity %
2' - 4'	33.4	19.0	18.0
4' - 6'	36.2	16.7	14.8
6' - 8'	32.4	19.9	14.4
8' - 10'	33.6	19.0	14.1
10' - 12'	32.6	19.8	13.8
12' - 14'	32.6	19.7	13.0
14' - 16'	32.8	19.6	13.8
16' - 18'	33.2	19.2	13.4
18' - 20'	33.6	18.9	15.2
20' - 22'	32.4	19.9	16.5
22' - 24'	33.2	19.2	12.6
24' - 26'	33.6	18.9	17.2
26' - 30'	35.6	15.7	15.5
30' - 32'	35.2	17.4	15.8
32' - 34'	37.6	15.0	15.5
34' - 36'	40.8	11.7	12.0
36' - 38'	37.0	15.2	15.2
38' - 42'	34.4	18.2	17.5
42' - 44'	34.4	17.9	15.2
44' - 46'	33.8	18.5	13.8
46' - 48'	34.0	18.4	12.0
48' - 50'	33.6	18.7	12.3
50' - 52'	32.4	19.7	11.6
52' - 54'	34.4	17.7	10.6
54' - 56'	34.8	17.8	15.2
56' - 58'	33.6	18.8	15.2
58' - 60'	38.0	14.9	14.8
60' - 62'	35.2	17.0	13.8
62' - 64'	34.4	17.2	14.1
64' - 66'	34.2	18.4	14.1
66' - 68'	34.2	18.4	16.2
68' - 70'	34.2	18.2	16.2
70' - 72'	34.0	18.6	16.2
72' - 74'	33.4	19.0	15.8
74' - 76'	33.0	19.3	15.2
76' - 78'	32.8	19.5	20.0
78' - 80'	32.0	20.2	20.4
80' - 82'	31.6	20.6	23.6
82' - 84'	32.0	20.3	19.0
84' - 86'	32.0	20.2	18.3
86' - 88'	33.0	19.4	19.0
88' - 90'	33.6	18.9	16.2
90' - 92'	32.6	19.7	16.2
92' - 94'	32.6	19.6	11.2
94' - 96'	32.2	20.0	15.5
96' - 98'	32.4	19.9	17.3
98' - 100'	32.8	19.4	14.8
100' - 102'	33.0	19.3	16.5
102' - 104'	32.6	19.5	16.2
104' - 106'	33.4	18.9	17.3
106' - 108'	33.8	18.5	20.0
108' - 110'	44.2	9.2	17.6
110' - 112'	32.4	18.6	12.3
112' - 114'	34.4	18.2	18.7
114' - 116'	32.4	19.8	18.0
116' - 118'	32.8	19.6	14.1
118' - 120'	32.4	19.9	16.9
120' - 122'	32.8	19.5	15.5
122' - 124' (2" clay excluded)	32.4	19.5	12.3
124' - 126'	33.0	19.2	12.0
126' - 128'	33.6	18.9	16.9
128' - 130'	33.2	19.1	18.7
130' - 132'	31.0	21.0	16.9
132' - 134'	33.2	19.3	18.3
134' - 136'	32.6	19.8	15.2
136' - 138'	33.2	19.2	24.7
138' - 140'	33.8	18.8	17.6
140' - 142'	34.4	18.2	15.5
142' - 144'	31.8	20.4	16.2
144' - 146'	31.8	20.5	18.3
146' - 148'	33.0	19.4	17.6
148' - 150'	32.2	20.1	16.5
150' - 152'	32.4	20.0	18.3
152' - 154'	34.2	18.6	16.5
154' - 156' (156' - 157' clay)	33.8	18.5	12.0
157' - 159'	32.4	19.6	12.0
159' - 161' (2" clay)	33.4	18.8	17.6
161' - 163' (163' - 163'8" clay)	32.8	18.8	16.5

HARBORS' BOREHOLE No. 7

Footage	CaO %	MgO %	Porosity %
4' - 7'	28.6	16.3	15.5
7' - 10'	33.0	19.2	16.5
10' - 13'	33.8	18.6	11.2
13' - 15'	34.0	18.4	10.9
15' - 17'	34.0	18.5	16.9
17' - 19'	34.0	18.5	18.3
(1" clay)			
19' - 22'	32.8	18.8	16.5
(22' - 25'			
25' - 27'	33.6	18.8	14.4
27' - 29'	33.2	19.2	14.4
29' - 31'	32.6	19.7	12.0
31' - 33'	33.2	19.3	13.4
33' - 35'	32.6	19.6	12.0
35' - 37'	31.8	20.4	11.2
37' - 39'	34.0	18.5	12.0
39' - 41'	32.4	20.0	12.0
41' - 43'	33.0	19.6	12.0
43' - 45'	46.6	2.8	10.5
(45' - 48'			
48' - 50'	39.8	13.1	9.9
50' - 52'	36.4	16.1	10.6
52' - 54'	33.4	19.0	10.6
54' - 56'	33.0	19.4	12.0
56' - 58'	31.8	20.2	12.0
58' - 60'	32.4	19.9	10.8
60' - 62'	32.8	19.5	10.6
62' - 64'	33.0	19.4	10.6
64' - 66'	32.2	20.0	10.8
66' - 68'	31.8	20.4	12.0
68' - 70'	31.4	20.7	9.2
70' - 72'	31.4	20.8	11.2
72' - 74'	32.0	20.2	11.2
74' - 76'	32.2	20.1	10.8
76' - 78'	32.2	20.0	10.6
78' - 80'	32.6	19.7	9.6
80' - 82'	32.6	19.7	9.9
82' - 84'	32.4	19.9	8.8
84' - 86'	32.2	20.0	9.2
86' - 88'	32.2	20.0	10.9
88' - 90'	32.4	19.8	10.9
90' - 92'	32.4	19.8	12.3
92' - 94'	32.2	20.0	13.8
94' - 96'	32.0	20.2	12.3
96' - 98'	34.0	18.4	13.8
98' - 100'	32.6	19.7	14.1
100' - 102'	32.2	19.2	15.2
102' - 104'	32.2	19.2	13.4
104' - 106'	32.2	19.2	13.4
106' - 108'	32.6	18.9	13.4
108' - 110'	34.0	18.6	12.7
110' - 112'	33.6	18.8	13.8
112' - 114'	33.6	18.8	12.0
114' - 116'	33.4	19.0	12.0
116' - 118'	33.6	18.9	10.2
118' - 120'	33.2	19.2	11.0
120' - 122'	33.2	19.2	9.2
122' - 124'	32.0	20.3	10.6
124' - 126'	33.6	19.0	10.6
126' - 128'	33.2	19.2	9.2
128' - 130'	34.0	18.4	12.7
130' - 132'	33.6	18.8	12.0
132' - 134'	33.2	20.2	11.0
134' - 136'	32.4	19.8	12.0
136' - 138'	33.2	19.2	10.6
138' - 140'	32.8	20.6	12.0
140' - 142'	32.8	20.6	12.0
142' - 144'	33.2	19.2	12.0
144' - 146'	33.2	19.2	12.0
146' - 148'	32.4	20.0	12.0
148' - 150'	32.0	20.4	12.0
150' - 152'	32.4	20.0	9.2
152' - 154'	32.4	20.0	10.2
154' - 156'	32.4	20.0	12.0
156' - 158'	39.6	13.8	16.2
(1'6" clay)			
159'6"-162'	30.8	19.6	18.7
162' - 164'	32.4	19.9	14.4
164' - 166'	33.2	19.2	13.8
166' - 168'	32.4	19.9	15.5

HARBORO' BOREHOLE NO . 8

Footage	CaO %	MgO %	Porosity %
0' - 2'	33.0	19.2	23.7
2' - 4'	33.2	18.9	21.5
4' - 6'	33.2	18.9	18.7
6' - 8'	32.0	20.2	18.7
8' - 10'	32.0	20.1	20.8
10' - 12'	32.4	19.8	18.0
12' - 14'	33.2	19.2	19.7
14' - 16'	32.6	19.7	21.8
16' - 18'	31.6	20.6	23.7
18' - 20'	31.4	20.8	20.1
20' - 22'	31.6	20.6	22.9
22' - 24'	32.4	19.9	22.2
24' - 26'	32.0	20.1	20.1
26' - 28'	32.4	19.6	18.7
28' - 20'	32.2	20.0	18.7
30' - 32'	32.2	20.2	22.2
32' - 34'	33.2	19.4	21.5
34' - 36'	34.0	18.6	19.7
36' - 38'	32.4	20.0	23.7
38' - 40'	32.2	20.2	23.7
40' - 42'	32.0	20.3	23.7
42' - 44'	33.2	19.3	20.8
44' - 46'	33.2	19.4	23.7
46' - 48'	32.6	19.8	20.8
48' - 50'	33.2	19.2	23.7
50' - 52'	31.6	20.4	23.7
52' - 54'	31.8	20.5	22.2
54' - 56'	31.0	21.1	23.7
56' - 58'	32.4	20.0	23.7
58' - 60'	32.6	19.9	20.4
60' - 62'	32.4	20.0	18.7
62' - 64'	31.6	20.6	19.7
64' - 66'	31.2	21.0	18.7
66' - 68'	33.4	19.2	16.6
68' - 70'	32.8	19.6	19.4
70' - 72'	32.0	20.3	19.0
(3" clay)			
72' - 74'	32.8	19.5	16.9
74' - 76'	32.0	19.8	20.4
76' - 78'	30.0	21.4	17.3
78' - 80'	30.4	19.8	16.6
80' - 82'	33.4	19.0	18.3
82' - 84'	30.6	20.9	15.9
84' - 86'	32.0	19.7	14.1
86' - 88'	32.2	19.7	15.1
88' - 90'	31.4	19.0	16.2
90' - 92'	31.6	19.25	15.1
92' - 94'	31.6	18.8	20.1
94' - 96'	34.2	17.8	19.4
96' - 98'	33.6	18.4	22.2
98' - 100'	33.4	18.8	21.8
100' - 102'	34.0	18.5	20.8
102' - 104'	33.0	19.4	19.4
104' - 106'	34.2	18.3	21.5
106' - 108'	37.4	15.5	16.6
108' - 112'5	23.0	11.3	
112'5" - 116'5	29.0	11.8	
(5'1" core)			
121'6" - 124'	33.6	18.8	22.9
124' - 126'	32.9	19.5	24.0
126' - 128'	33.7	18.8	21.8
128' - 130'	32.5	19.9	21.5
130' - 132'	32.7	19.6	16.6
132' - 134'	32.5	19.9	17.7
134' - 136'	31.3	20.9	16.2
136' - 138'	33.5	19.0	13.4
138' - 140'	33.3	19.1	13.4
140' - 142'	34.3	17.8	12.7
142' - 144'	33.9	18.6	18.3
144' - 146'	33.7	18.8	22.2
146' - 148'	32.9	19.4	20.1
148' - 150'	32.5	19.7	19.4
150' - 152'	31.9	20.4	21.8
152' - 154'	32.1	20.2	19.4
154' - 156'	32.1	20.2	18.0
156' - 158'	32.5	19.8	18.3
158' - 160'	32.1	19.9	18.3
160' - 162'	32.1	20.3	17.7

HARBORO' BOREHOLE No. 9

Footage	CaO %	MgO %	Porosity %
(Sand 2'6" - 12'9")			
12'9" - 14'	30.9	20.8	20.1
14' - 16'	31.7	20.2	14.8
16' - 18'	32.1	20.1	13.4
18' - 20'	32.1	20.1	13.4
20' - 22'	33.7	18.8	14.1
22' - 24'	32.9	19.5	13.0
24' - 26'	32.5	19.8	13.8
26' - 28'	32.2	20.0	16.6
28' - 30'	32.0	20.2	16.2
30' - 32'	32.0	20.2	20.1
32' - 34'	32.6	19.7	15.5
34' - 36'	32.0	19.8	12.0
(10" clay)			
36' - 38'	31.6	19.5	9.9
38' - 40'	33.2	19.2	16.2
40' - 42'	33.6	18.7	15.9
42' - 44'	31.8	20.2	18.0
44' - 46'	31.6	20.4	17.7
46' - 48'	32.4	19.9	15.9
48' - 50'	32.6	19.7	15.5
50' - 52'	33.2	19.2	15.9
52' - 54'	32.6	19.6	17.7
54' - 57'5"	33.5	18.8	15.9
(57'5" - 61'9" cavity)			
61'9" - 64'	31.7	20.4	21.5
64' - 66'	32.1	19.8	17.5
66' - 68'10"	31.7	20.4	18.7
71'2" - 74'	33.5	18.9	16.2
74' - 76'	34.9	17.0	15.9
76' - 78'	35.7	17.0	13.8
78' - 80'	34.9	17.6	16.2
80' - 82'	31.7	20.4	20.1
82' - 83'3"	33.7	18.7	18.7
(83'3" - 138'2" Cavity)			
138'2" - 140'	29.7	2.8	12.0
140' - 142'	23.9	2.8	15.1
(142' - 157' Sand no Sample)			
157' - 158'	32.1	18.2	14.4
(158' - 162'6" Sand no Sample)			

HARBORO' BOREHOLE No. 10

Footage	CaO %	MgO %	Porosity %
2' - 4'	31.7	20.5	18.7
4' - 6'	31.7	20.5	16.6
6' - 8'	31.1	21.0	18.7
8' - 10'	31.9	20.4	20.1
10' - 12'	31.7	20.5	21.8
12' - 14'	32.3	20.0	18.7
14' - 16'	31.9	20.3	18.0
16' - 18'	31.1	19.6	21.2
18' - 20'	30.9	21.1	20.8
20' - 22'	30.7	21.0	21.5
22' - 24'	30.7	21.2	15.9
24' - 26'	32.1	20.1	18.3
26' - 28'	32.9	19.5	18.0
28' - 30'	32.7	19.6	18.7
30' - 32'	31.7	20.4	18.0
32' - 34'	32.1	20.2	16.9
34' - 36'	30.7	21.4	15.9
36' - 38'	31.7	20.5	12.3
38' - 40'	32.9	19.4	15.5
40' - 42'	33.3	19.2	18.3
42' - 44' (6" clay excluded)	32.5	19.8	18.3
44' - 46'	31.9	20.2	15.5
46' - 48'	31.9	20.2	21.2
48' - 50'	30.9	20.9	20.1
50' - 52'	30.5	21.0	20.4
52' - 54'	31.3	20.8	19.0
54' - 56'	33.9	18.6	18.0
56' - 58'	31.9	20.4	18.3
58' - 60'	32.7	19.5	18.3
60' - 62'	32.0	20.0	19.7
62' - 64'	32.6	19.6	18.0
64' - 66'	32.0	20.1	16.9
66' - 68'	31.8	20.3	18.3
68' - 70'	32.2	20.0	18.7
70' - 72'	31.8	20.4	21.2
72' - 74'	32.0	20.3	19.0
74' - 76'	31.6	20.6	19.4
76' - 78'	32.0	20.4	20.1
78' - 80' (8" clay excluded)	32.6	19.7	20.1
80' - 82'	31.6	18.7	20.8
80' - 82'	31.6	20.6	21.2
82' - 84'	32.0	20.3	22.9
84' - 86'	31.2	21.0	22.5
86' - 88'	32.4	20.0	20.1
88' - 90'	31.6	20.6	23.7
90' - 92'	31.6	20.6	24.3
92' - 94'	32.2	20.2	23.3
94' - 96'	31.6	20.7	20.8
96' - 98'	32.2	20.2	19.7
98' - 100'	32.0	20.4	20.1
100' - 102'	32.0	20.3	18.7
102' - 104'	31.4	20.8	20.8
104' - 106'	30.8	21.5	19.7
106' - 108'	31.8	20.6	19.7
108' - 110'	33.2	19.4	21.5
110' - 112'	30.8	19.3	18.3
112' - 114'	32.8	19.2	16.6
114' - 116'	33.2	19.0	16.6
116' - 118'	31.6	19.1	18.7
118' - 120'	32.0	20.0	19.4
120' - 122'	31.6	20.6	20.8
122' - 124'	32.8	19.6	19.0
124' - 126'	32.0	20.3	20.8
126' - 128'	32.2	20.0	18.7
128' - 130'	32.4	20.0	22.2
130' - 132'	33.2	19.2	22.9
132' - 134'	33.2	19.3	22.2
134' - 136'	32.2	20.1	21.5
136' - 138'	32.0	20.3	20.8
138' - 140'	32.6	19.8	19.4
140' - 142'	32.4	19.6	18.0
142' - 144'	32.0	20.0	14.8
144' - 146'	32.6	19.6	15.5
146' - 148'	33.4	18.4	14.4
148' - 150'	32.0	20.1	16.9
150' - 152'	33.2	19.1	17.7
152' - 154'	32.2	19.8	19.0
154' - 156'	32.6	19.7	19.0
156' - 158'	33.0	19.3	20.4
158' - 160'	31.8	20.4	16.9
160' - 162'	32.6	19.8	16.9

HARBORO' BOREHOLE No.11

Footage	CaO %	MgO %	Porosity %
2-4'	31.8	20.0	19.0
4-6'	32.6	19.6	16.9
6-8'	34.0	18.2	12.3
8-10'	33.6	18.9	12.3
10-12'	34.2	18.1	15.5
12-14'	34.0	18.3	14.8
14-16'	34.0	18.3	12.3
16-18'	34.0	18.4	14.4
18-20'	32.8	19.5	17.7
20-22'	32.8	19.4	17.7
22-24'	32.4	19.9	19.0
24-26'	32.4	19.9	20.4
26-28'	31.2	20.7	17.7
28-30'	32.8	19.4	16.6
30-32'	32.4	19.9	15.5
32-34'	32.0	20.2	15.9
34-36'	32.0	20.2	15.9
36-38'	31.6	20.7	18.3
38-40'	31.2	20.9	16.9
40-42'	31.4	20.9	17.3
42-44'	32.0	20.1	16.2
44-46'	31.6	20.6	15.9
46-48'	32.0	20.2	13.4
48-50'	31.8	20.5	16.9
50-52'	32.4	19.9	13.4
52-54'	32.2	20.0	16.6
54-56'	31.6	20.4	16.6
56-58'	31.6	20.6	12.0
58-60'	34.0	20.4	13.4
60-62'	32.0	20.5	14.4
62-64'	32.6	19.6	12.7
64-66'	32.2	20.1	14.4
66-68'	31.2	21.1	16.9
68-70'	31.8	20.3	13.4
70-72'	31.8	20.3	13.4
72-74'	32.6	19.6	13.4
74-76'	31.8	20.4	12.0
76-78'	32.0	20.3	12.7
78-80'	32.6	19.8	13.8
80-82'	32.9	19.6	15.9
82-84'	32.8	19.6	16.2
84-86'	33.4	18.9	14.1
86-88'	33.6	18.0	9.5
88-90'	33.6	18.0	9.5
90-92'	32.0	20.1	13.4
92-94'	31.8	20.6	14.1
94-96'	32.0	20.3	17.3
96-98'	32.0	20.3	16.2
98-100'	31.8	20.4	9.9
100-102'	32.4	19.8	9.2
102-104'	32.0	20.1	9.9
104-106'	33.0	20.1	7.1

HARBORO' BOREHOLE No12

Footage	CaO %	MgO %	Porosity %
30-32'	32.8	19.5	13.4
32-34'	32.6	19.6	13.8
34-36'	32.4	19.5	10.2
36-38'	33.0	19.3	12.0
38-40'	32.8	19.6	13.8
40-42	33.2	19.1	13.4
57-60'	33.0	19.4	11.7
60-62'	33.6	18.9	12.3
62-64'	33.2	19.2	13.4
64-66'	31.4	20.7	15.5
66-68'	32.4	19.5	10.2
68-70'	34.0	18.6	10.6
70-72'	32.4	18.9	16.2
72-74'	33.8	18.9	11.0
74-76'	33.6	18.9	9.9
76-78'	34.2	18.3	10.6
78-80'	34.4	18.3	11.3
80-82'	34.2	18.4	10.6
82-84'	33.4	19.0	14.4
84-86'	33.8	18.8	11.3
86-88'	35.0	17.5	11.7
88-90'	35.0	17.2	9.5
90-92'	32.0	20.4	9.2
92-94'	32.4	20.0	10.2
94-97'	31.2	21.7	12.0
98-100'	31.6	20.5	12.0
100-102'	33.4	19.3	12.3
102-104'	33.0	19.5	11.7

HARBORO' BOREHOLE No13

Footage	CaO %	MgO %	Porosity %	Footage	CaO %	MgO %	Porosity %
4-6'	32.6	18.9	12.0	60-62'	32.0	20.1	11.0
6-8'	33.6	18.5	12.7	62-64'	32.0	20.1	8.1
8-10'	34.0	18.4	12.7	64.66'	32.4	19.9	9.2
10-12'	31.0	21.0	20.1	66-68'	31.6	20.3	9.5
12-15'	31.0	20.8	19.4	68-70'	34.6	17.9	12.3
15-17'	33.2	18.8		70-72'	32.4	19.8	13.4
17-19'	31.4	17.9	12.7	72-74'	33.8	18.6	11.0
19-21'	34.0	18.3	12.3	74-76'	33.0	18.9	13.4
21-23'	34.3	18.1	11.0	76-78'	35.6	17.1	10.2
23-25'	32.0	20.3	15.5	78-80'	35.0	17.5	11.3
30-32'	33.4	18.9	14.4	80-82'	33.4	18.7	11.7
32-34'	33.2	19.0	15.9	82-84'	33.4	18.9	11.7
34-36'	33.0	19.1	12.7	84-86'	32.4	19.8	10.2
36-38'	33.8	18.4	10.6	86-88'	32.4	19.8	12.3
38-40'	32.8	19.3	12.7	88-90'	33.2	19.2	11.0
40-42'	32.6	19.4	13.0	90-91'	33.0	19.4	12.7
42-44'	33.6	18.1	10.6	98-100'	32.0	20.3	8.5
44-46'	34.0	18.1	9.9	100-102'	32.4	19.9	12.3
46-48'	33.2	19.2	10.2	102-104'	31.8	20.3	14.1
48-50'	32.2	19.5	11.3	104-106'	32.6	19.5	14½1
50-52'	32.2	19.5	11.0	106-108'	32.4	19.9	12.3
52-54'	32.2	19.0	12.1	108-110'	34.2	18.3	12.7
54-56'	31.4	19.0	9.2	110-112'	34.0	18.5	12.3
56-58'	32.0	20.1	8.8	112-114'	31.0	21.0	15.9
58-60'	31.8	20.2	8.8	114-116'	31.2	20.4	14.1

HARBORO' BOREHOLE No.14

Footage	CaO %	MgO %	Porosity %
2-4'	33.4	18.9	15.9
4-6'	33.5	18.8	14.8
6-8'	32.7	19.8	14.1
8-10'	34.2	18.3	14.8
10-12'	33.6	18.9	13.4
12-14'	32.6	19.8	13.4
14-16'	33.6	19.0	13.0
16-18'	45.2	8.7	12.3
18-20'	54.4	0.5	11.0
20-22'	37.2	15.7	13.0
22-24'	35.4	17.3	15.5
28-30'	33.4	18.9	15.5
30-32'	33.2	19.2	12.7
32-34'	33.4	19.0	13.8
34-36'	33.4	19.0	13.0
36-38'	34.4	17.9	12.7
38-40'	33.8	18.6	14.8
40-42'	32.8	19.4	14.1
44-46'	33.2	19.0	14.4
46-48'	33.6	18.6	13.0
48-50'	33.6	18.8	13.0
50-52'	34.2	17.7	13.8
52-54'	33.0	19.2	14.8
54-56'	32.8	19.4	13.8
56-58'	32.4	19.7	12.7
58-60'	32.3	19.4	12.7
60-62'	33.4	18.8	12.0
62-64'	32.8	19.3	14.8
64-66'	32.6	19.6	13.8
66-68'	33.0	19.4	13.8
68-70'	32.6	19.7	13.8
70-72'	32.2	20.0	12.3
72-74'	34.0	18.5	12.0
74-76'	34.6	17.9	14.4
76-78'	34.8	17.9	13.8
78-80'	39.4	14.0	17.7
80-82'	49.0	2.4	7.1
82-84'	53.0	1.3	11.3
84-86'	50.4	4.2	15.1
89-91'	33.4	18.8	12.3
91-93'	32.6	19.6	9.2
93-95'	33.8	18.6	9.5
95-97'	36.2	16.6	13.4
97-99'	34.6	18.1	11.7
99-101'	34.2	18.4	12.7
101-103'	35.4	17.3	13.0
103-105'	34.8	17.9	13.0
105-107'	35.8	16.9	13.4

HARBORO' BOREHOLE No.15

Footage	CaO %	MgO %	Porosity %
0-2'	32.6	19.6	12.7
2-4'	33.0	19.3	13.4
4-6'	32.2	20.2	14.1
6-8'	32.6	19.8	12.0
8-10'	39.2	14.1	13.4
10-12'	33.6	18.9	10.2
12-14'	34.2	17.8	8.1
14-16'	31.4	20.3	5.7
16-17'	30.9	20.2	5.7
20-22'	32.0	20.1	12.0
22-24'	32.0	20.0	11.0
24-26'	36.0	16.7	14.1
26-28'	31.6	20.6	12.7
28-30'	35.0	17.7	15.9
30-32'	34.8	17.0	13.4
34-36'	32.2	19.8	15.5
36-38'	30.8	20.9	15.5
38-40'	32.6	19.3	12.7
40-42'	31.8	19.8	11.7
42-44'	33.2	18.1	11.3
44-46'	32.6	19.5	7.8
46-48'	34.0	18.2	11.0
48-50'	34.4	17.7	9.9
50-52'	33.2	19.1	13.5
52-54'	32.6	19.3	16.6
54-56'	33.4	19.4	18.0
56-58'	33.4	18.2	15.9
58-60'	33.2	18.9	15.5
60-62'	33.0	19.1	14.4
62-64'	31.8	20.3	14.1
64-66'	32.2	19.9	12.3
66-68'	32.2	19.9	11.0
68-70'	31.4	20.5	10.2
70-72'	31.8	20.2	14.8
72-74'	34.2	18.2	9.5
74-76'	34.4	18.1	14.8
76-78'	34.0	18.5	11.7
78-80'	32.6	19.5	7.8
80-82'	33.8	18.5	6.7
82-84'	32.6	20.2	7.8
84-86'	32.2	17.9	8.8
86-88'	32.2	19.2	8.1
88-90'	32.2	20.0	9.5
90-92'	32.2	20.0	11.7
92-94'	33.0	19.3	12.3
94-96'	32.6	19.5	11.3
96-98'	33.2	19.2	11.0
98-100'	34.0	18.4	11.0

HARBORO' BOREHOLE No.16

Footage	CaO %	MgO %	Porosity %
2-8'	30.8	21.3	13.8
8-11'	31.2	20.8	16.6
11-13'	31.6	20.4	22.9
13-15'	32.8	19.4	20.8
15-17'	36.0	16.7	16.9
17-19'	36.0	16.8	15.1
19-21'	36.0	16.7	15.1
21-23'	34.8	17.9	16.2
23-25'	34.0	18.6	15.2
25-27'	31.8	20.4	13.4
27-29'	31.6	20.6	8.5
29-31'	32.4	19.7	8.8
31-33'	32.0	19.2	7.8
33-35'	31.6	20.0	15.9
35-37'	32.4	19.7	16.2
37-39'	32.0	20.1	15.9
39-41'	31.6	20.5	17.7
41-43'	30.8	21.1	15.9
43-45'	32.0	19.9	15.9
45-47'	31.2	20.8	16.6
47-49'	31.6	20.5	14.8
49-51'	32.2	20.0	12.0
51-53'	33.8	18.4	12.0
53-55'	31.8	19.0	18.3
55-57'	31.6	20.0	14.8
57-59'	32.6	19.6	14.1
59-61'	32.0	20.2	11.7
61-63'	32.0	20.2	9.5
63-65'	31.8	20.4	12.0
65-67'	31.8	20.4	13.0
67-69'	31.4	20.4	12.0
69-71'	31.4	20.8	11.7
71-73'	31.6	20.6	12.0
73-75'	31.6	20.6	12.0
75-77'	31.6	20.5	9.5
77-79'	31.2	20.5	9.5
79-81'	31.2	20.9	12.0
81-83'	30.8	21.3	11.0
83-85'	32.0	20.2	13.0
85-87'	31.6	20.6	12.0
87-89'	30.8	21.3	9.5
89-91'	31.6	20.6	11.7
91-93'	31.2	21.6	11.0
93-95'	30.8	21.4	9.5
95-97'	32.4	19.8	12.0
97-99'	32.0	20.1	12.0
99-101'	32.4	19.8	9.5
101-103'	31.6	20.6	12.0

HARBORO' BOREHOLE NO.17

Footage	CaO %	MgO %	Porosity %	Footage	CaO %	MgO %	Porosity %
2-6'	34.2	15.38	16.9	80-82'	34.4	18.04	11.7
6-8'	32.8	18.44	12.0	82-84'	35.6	17.02	12.3
8-10	34.8	16.83	14.3	84-86'	34.4	17.24	13.8
10-12'	32.6	18.99	14.1	86-88'	36.0	16.24	13.8
12-14'	33.0	19.0	14.1	88-90'	34.2	18.18	10.2
14-16'	32.4	19.37	16.9	90-92'	34.8	17.68	9.5
16-18'	32.6	19.0	12.0	92-94'	37.2	15.80	9.5
18-20'	32.8	19.02	16.9	94-96'	35.4	17.68	13.0
20-22'	32.6	19.47	14.1	96-98'	36.0	16.60	16.9
22-24'	33.0	19.11	14.1	98-100'	34.4	17.86	14.8
24-26'	34.4	17.36	13.0	100-102'	35.2	16.71	14.1
26-28'	34.6	17.29	10.2	102-104'	35.6	17.00	14.1
28-30'	36.6	14.77	6.4	104-106'	34.0	18.61	13.8
30-32'	37.0	14.92	8.8	106-108'	34.0	18.22	13.8
32-34'	32.2	19.84	14.1	108-110'	34.0	18.14	13.0
34-36'	33.4	18.29	12.0	110-112'	34.4	17.72	13.4
36-38'	33.2	18.64	8.5	112-114'	33.2	18.90	11.3
38-40	34.0	18.48	10.6	114-116'	33.8	18.44	11.0
40-42'	34.0	18.30	11.0	116-118'	34.4	17.98	10.6
42-44'	34.4	17.16	12.0	118-120'	32.8	19.08	11.7
44-46'	34.8	1734	12.0	120-122'	33.6	18.72	12.3
46-48'	33.6	18.61	12.0	122-124'	33.6	19.00	8.1
48-50'	38.4	14.74	13.0	124-126'	32.0	18.72	11.7
50-52'	33.2	19.22	13.0	126-128'	31.6	18.65	12.7
52-54'	33.6	18.82	11.3	128-130'	31.6	19.26	12.3
54-56'	34.0	18.11	14.1	130-132'	31.6	19.69	10.2
56-58'	36.0	16.63	14.1	132-134'	31.6	20.44	10.2
58-60'	34.8	17.82	12.0	134-136'	31.2	20.70	8.8
60-62'	34.0	18.58	9.5	136-138'	32.8	19.20	10.2
62-64'	40.0	13.93	12.0	138-140'	29.6	18.69	9.5
64-66'	41.2	11.11	8.1	140-142'	30.4	20.40	11.3
66-68'	37.2	15.20	7.1	142-144'	30.6	21.14	11.7
68-70'	37.6	13.73	7.1	144-146'	30.0	21.28	11.7
70-72'	40.0	12.65	11.0	146-148'	29.8	19.08	10.2
72-74'	34.8	17.70	6.7	148-150'	28.4	19.18	6.4
74-76'	36.8	15.88	11.0	150-152'	30.0	20.12	12.7
76-78'	37.2	15.58	11.3	152-154'	31.0	20.88	13.0
78-80'	34.4	18.10	10.6	154-156'	30.6	21.52	9.5

HARBORO' BOREHOLE NO.17 (cont'd)

Footage	CaO %	MgO %	Porosity %
158-160'	31.8	20.22	8.1
160-162'	31.2	20.90	10.2
162-164'	33.2	19.32	8.1
164-166'	33.2	19.20	11.0
166-168'	31.6	20.60	9.5
168-170'	31.2	20.90	11.0
170-172	29.6	22.32	9.9
172-174'	31.2	20.80	11.0
174-176'	31.2	20.80	12.0
176-178'	30.8	21.28	10.2
178-180'	31.4	20.68	11.0
180-182'	31.8	20.30	14.4
182-184'	31.8	20.20	15.5
184-186'	31.2	20.70	16.2
186-188'	32.6	19.50	12.7
188-190'	31.4	20.60	13.0
190-193'	32.2	19.80	15.5
194-196'	31.8	20.20	10.2

APPENDIX V

Atomic Absorption Spectroscopy

The Technique

Atomic Absorption Spectroscopy is a technique for measuring the concentration of particular elements in solution. The method involves aspirating the solution through a nebuliser where the solution droplets are atomised and mixed with a combustible gas mixture (usually air-acetylene, air-propane or nitrous oxide-acetylene). This aerosol mixture is burnt as a flame. The energy of the flame is used to evaporate the aerosol particles, 'ash' the salts remaining and decompose these salts releasing their constituents as atoms. Atoms of different elements absorb light of characteristic wave-length in the UV-visible part of the spectrum. Atomic Absorption measurements are made by passing light of that characteristic frequency through the flame and measuring the amount absorbed. This absorbed light is proportional to the concentration of the element present in the flame and hence in the aspirated solution. By comparing the absorption of unknown solutions with solutions containing a known (standard) amount of the element, the unknown concentration may be calculated.

The low concentrations of Na^+ and K^+ in these carbonates do not allow these elements to be analysed by the normal E.D.X.r.f. method (Appendix IV). The detection limits of this equipment are 0.0003ug/ml for Na^+ and 0.003ug/ml for K^+, both of which are far below the concentrations found in these carbonates.

Sample Preparation

Whole rock limestone and dolostone, and constituent calcite and dolomite, were analysed. The constituent calcite and dolomite were obtained by leaching with either acetic or nitric acid.

1) Whole Rock Analysis

0.2g of whole rock limestone and dolostone were fused with the flux lithium metaborate (2g) in a furnace at 900°C. The fused mixture was then dissolved in 5% nitric acid and made up to 100ml. with deionised water. This method of dissolution serves two purposes; (i) it prevents silica precipitating out which frequently occurs during the more usual HF acid dissolution and (ii) the presence of lithium in the solution minimises the ionisation of sodium in the flame. The signal obtained from the unknown is directly compared to standard solutions of known concentrations. A control solution of just the additives was also analysed to account for any contamination that may be introduced during preparation.

2) Constituent calcite and dolomite

Limestone samples were dissolved in dilute acetic acid, and the resultant solution separated from the insoluble residue. The solution was evaporated to dryness. The residue was crushed and 0.2g of the powder, together with 2g of lithium metaborate was dissolved in deionised water and made up to 100ml.. The solutions were analysed in a similar manner to that above.

Dolostone samples were firstly dissolved in dilute acetic acid to remove the excess calcite, which is commonly associated with the dolostone. The solution was removed and the remaining dolomite washed. The dolomite was dissolved in dilute nitric acid and the resultant solution decanted from the insoluble residue. The solution was evaporated almost to dryness, but due to the deliquescent nature of the nitrate it never crystallises. The mush was then calcined and the resultant oxide was dissolved in the necessary flux in the same way as described above.

Sodium Concentrations (p.p.m.)

SAMPLE NO.	Wh. Rock	Calcite	Dolomite
H.R.	258	201	235
1A*	231	77	---
1C*	227	171	---
1D*	264	---	247
10E	30	88	---
10B*	170	65	---
1mas.	270	228	291
130-133	187	229	244
8A*	46	66	---
8C	175	174	322
8F*	42	79	---

* limestone samples

Potassium Concentrations (p.p.m.)

SAMPLE NO.	Wh. Rock	Calcite	Dolomite
H.R.	91	57	76
1A*	503	47	---
1C*	227	63	---
1D	410	103	144
10E	48	63	---
10B*	78	51	---
1mas.	109	55	57
130-133	128	43	76
8A*	299	38	---
8C	93	47	102
8F*	53	47	---

* limestone samples

A P P E N D I X V I

Energy Dispersive X-R-F

The Technique

Major and trace element analysis of rock samples is performed with a Link Systems Meca 10-44 Energy Dispersive X-ray Fluorescence Spectrometer, on glass fusion discs and pressed rock pellets respectively. Up to twenty samples may be analysed automatically without operator intervention. They are fluoresced using a low power (45 watt max.) silver side-window tube, normally operated in pulse mode to maximise counting throughput. A selection of five filters may be inserted in the primary beam to modify the energy distribution of the incident beam. The plane of the collimator of the X-ray source and the Si(Li) detector is at right angles to the sample surface and arranged so that the incident beam and the fluorescent X-rays to be detected are at 45^{o} to the sample surface.

Fluorescent X-rays are processed by the Link Systems 860 Analyser System and displayed as an X-ray energy spectrum which is recorded on floppy disc for subsequent spectral deconvolution and peak integration. A 2010 Harwell Processor comprises part of the Analyser System and handles base-line restoration, pulse-pile up rejection and sets a "strobe" peak at zero energy to facilitate spectrum processing. At the start of every run the spectrum gain is measured by recording a peak of known energy. Once set, when deconvolution of subsequent spectra is performed an autocalibration routine checks for system gain, drift and makes necessary adjustments to the gain value used in the deconvolution.

Spectra are recorded over 1024 channels at 10, 20 or 40eV per channel, depending on the energy range of interest. System resolution is 165eV FWHM for MnK_{α} at 5.9KeV when operating the main amplifier at 20μsec. processing time. The system is calibrated for count rate dependent upon spectral distortions, which is minimal at count rates below 10k.c.p.s.. All major elements are adequately analysed at 10kV, but sensitivity is poor for the highest elements, especially Na. Trace elements are analysed at 15kV.

Spectral deconvolution, filtered least squares fitting, is carried out, not only for elements on which data are to be quantified, but also for some additional lines which interfere with those of interest. Peak counts are directly compared to standard peaks for each individual element, upon which the system is calibrated. A summary of the compositions of the standard used in this study are given in the following tables. G.F.S. standards were used for the major elements, whilst due to the lack of suitable standards for trace elements, synthetic standards produced in the Department were used.

Sample Preparation

Only whole rock limestone and dolostone were analysed using this method. The analysis of the majors and traces were performed separately and thus different preparations are required.

(1) Majors.

A known amount (approximately 1g.) of rock powder was

placed in a silica crucible and heated in a furnace at 1100°C for 20 mins., which gave the oxide. The remaining oxide was weighed to determine the Loss on Ignition (L.O.I.) for the sample. The oxide was then crushed and 0.4g. of this powder was added to 2.4g. of Spectroflux 100B and fused in the furnace at 1100°C. The molten material was then pressed into a glass bead and allowed to cool.

(2) Traces.

6g. of powdered rock sample were mixed thoroughly with six drops of the binding agent Moviol. The mixture was then pressed into a pellet.

		Detection Levels	Detection Limits
Majors:	Ca	0.2%	0.1%
	Mg	0.2%	0.1%
	Fe	0.1%	0.05%
	Si	0.1%	0.05%
	Al	0.1%	0.1%
Traces:	Y	5p.p.m.	5p.p.m.
	Sr	10p.p.m.	10p.p.m.
	Mn	100p.p.m.	30p.p.m.
	Zn	5p.p.m.	5p.p.m.
	Pb	10p.p.m.	10p.p.m.
	Br	15p.p.m.	10p.p.m.

Majors

Standard	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	L.O.I.	Total
G.F.S. 400	0.06	0.04	0.08	30.45	21.59	0.01	0.02	47.41	99.74
G.F.S. 401	1.98	0.25	0.25	50.41	3.60	0.01	0.04	43.32	99.95
G.F.S. 402	2.59	0.59	0.40	46.78	5.81	0.01	0.07	43.09	99.48
G.F.S. 404	1.17	0.29	1.15	38.52	13.47	0.01	0.04	45.00	99.74
G.F.S. 406	0.65	0.14	0.13	34.66	17.60	0.01	0.03	46.39	99.71
G.F.S. 407	1.72	0.50	0.70	42.83	9.49	0.01	0.04	44.27	99.64
G.F.S. 410	0.85	0.17	0.16	36.48	15.77	0.01	0.03	46.09	99.62
G.F.S. 412	1.26	0.17	0.37	36.51	15.41	0.02	0.06	45.67	99.57
G.F.S. 415	0.55	0.09	0.15	32.82	19.32	0.01	0.02	46.75	99.81
G.F.S. 417	2.83	0.60	0.48	44.30	7.60	0.01	0.09	43.11	99.21

Traces - synthetic standards

Standard	Y	Br	Mn	Pb	Zn	Sr	Zr
Pellet 1.	5.8	21.7	46.6	13.0	5.7	48.9	9.8
Pellet 2.	3.9	18.4	39.7	10.9	5.9	55.6	5.8
Pellet 3.	13.9	25.8	173.5	35.7	26.2	75.8	31.6
Pellet 4.	7.3	18.5	110.4	19.7	16.5	78.7	15.1
Pellet 5.	17.3	32.4	262.3	29.6	32.3	100.2	27.3
Pellet 6.	15.8	20.1	244.8	28.0	24.9	125.1	25.7
Pellet 7.	19.2	24.4	540.8	55.7	50.3	150.8	53.3
Pellet 8.	19.0	24.4	553.5	45.1	56.1	162.3	53.2
Pellet 9.	24.1	13.1	1220.0	68.2	75.1	302.3	77.2
Pellet 10.	23.1	13.1	1231.0	69.6	74.5	297.2	76.5
Pellet 11.	28.2	96.4	1984.0	88.0	93.5	440.7	95.1
Pellet 12.	31.6	125.9	2135.0	98.9	122.9	462.3	107.1
Pellet 13.	40.1	144.3	2987.0	158.2	146.2	603.1	145.3
Pellet 14.	40.1	140.9	3074.0	157.8	151.2	621.2	150.4
Pellet 15.	50.2	159.0	4061.0	-----	205.1	807.8	203.9
Pellet 16.	49.7	244.1	3886.0	-----	194.8	796.8	204.5

A P P E N D I X V I I

Summary Description of Instrumental Neutron Activation Analysis at the Open University.

Powdered rock samples (0.3g.) are sealed in polythene capsules and irradiated in batches of 10 at the University of London Reactor Centre, Ascot. Each batch consists of an irradiation standard rock (Ailsa Craig microgranite) and a second calibration standard (usually a standard rock from Flanagan's 1973 or 1976 compilations) and eight unknowns. Each sample is separated by an iron foil used to measure the neutron flux variation between standard and unknowns. After irradiating in a flux of approximately 10^{12} neutrons $cm^{-2}sec^{-1}$ for 25 to 30 hours (one week of reactor time) samples are allowed to "cool" down for a further week in order to allow the intense short half-life activity due to Al, Na, Mn to decay away.

Samples are then returned to the Open University and the gamma spectra counted in two stages using two Ge(Li) detectors, a 4096 channel analyser and paper tape output, giving digital spectra of 1024 channels each.

1) The first stage is to count the short lived activity due to La and Sm. Sm is determined by counting the 60-150 keV spectrum on the LEPS detector for 800 seconds for each sample in a batch. La is determined in the 800-1600 keV spectrum on the coaxial detector, again each sample being counted for 800 seconds. It is convenient to simultaneously determine Sc, Fe and Co in the latter spectra. Peak areas are found by direct integration

of selected regions representing peak + background and adjacent background using the integrate facility available on the Multichannel Analyser.

Peaks used for determination are:-

Peak Energy KeV	Isotope
103.2	Sm^{153}
1596.6	La^{140}
889.3	Sc^{46}
1291.5	Fe^{59}
1332.5	Co^{60}

Integrated data from the MCA are fed into a simple program which corrects peak areas for background counts, neutron flux variations, weight of sample and exponential decay, and calculates p.p.m. by comparison with the Ailsa Craig Radiation Sample. Sc is usually determined relative to the second irradiated standard. The Pa 103.8 keV on Sm is monitored.

2) The second stage is to recount each sample sequentially, recording the 60-150 keV spectrum on the LEPS detector to determine the abundances of remaining detectable REE and certain other elements. Spectra are counted for at least $\frac{1}{4}$ of a day (20,000 seconds) and photopeaks can be detected down to about 0.05 counts per second per gram of sample.

Isotopes detected are as follows:-

Peak Energy KeV	Isotope	Peak Energy KeV	Isotope
63.1	Yb^{169}	109.8	Yb^{169}
67.7	Ta^{182}	112.9	Lu^{177}
84.3	Tm^{170}	121.7	Eu^{152}
86.8	Ta^{160}/Pa^{233}	123.8	Ba^{131}
91.1	Nd^{147}	130.5	Yb^{169}
93.6	Yb^{169}	133.1	Hf^{181}
94.7	Pa^{233*}	136.3	Hf^{181}
97.4	Gd^{153}/Sm^{153}	136.9	Hf^{181}
98.4	Pa^{233*}	145.4	Ce^{141}
100.1	Ta^{182}	152.3	Ta^{182}
103.2	Gd^{153}/Sm^{153}		

* for Th. determinations

Spectra data are recorded as 1024 channel spectra on paper tape.

Peak areas of interest are calculated using the least squares peakfitting program SAMPO (see Routti 1969), and areas are corrected for count time, weight of sample, exponential decay and neutron flux variations. Corrections for isotope interferences are calculated for peaks at 86.8 (Tb/Pa), 97.4 (Gd/Sm) and 103.2 (Gd/Sm) keV. Peak areas then compared with those in the Ailsa Craig irradiation standard to determine p.p.m.. Ba is usually determined by comparison with the second standard.

Neutron flux corrctions are determined by measuring the specific activity of each iron foil in a 300 second count on the coaxial detector. This allows corrections to be made to sample p.p.m. for flux variations in the reactor over the length of an irradiation can.

Computer processing of gamma spectra is fully described in "Determinations of Rare Earth and Other Elements by I.N.A.A. at the Open University" (2nd Edition June 1978, by Dave Wright, Open University).

Precision and detection limits vary with length of irradiation, height of background spectrum and length of time elapsed since irradiation.

Sample Preparation

Whole rock, constituent carbonate and clays were all analysed by I.N.A.A.. The carbonates and clays were obtained by controlled leaching experiments using acetic or nitric acid, with or without the addition of E.D.T.A.. The E.D.T.A. under specific conditions was believed by Spirn (1965) to prevent any excess leaching of loosely-bound REE (Rare Earth Elements) on the surface of the clay minerals, during dissolution.

1) Analysis of the Limestone

A series of whole rock limestone, clacite leachate and clays were analysed. The leachates were obtained by dissolving the limestones in 10% acetic acid, with the

addition of 1% E.D.T.A. and keeping the pH 4 (following Spirn 1965). To study the effect of the E.D.T.A. during dissolution, dissolution experiments were performed, without the use of E.D.T.A.. This is discussed in Section 7.2.6.

Following the dissolution of the limestone, the leachate was allowed to settle and the solution was then pipetted off, leaving the clays behind. The leachate solution was evaporated to dryness and the powder analysed following the procedure outlined in the first part of this Appendix. The total dissolution of the limestone gave the insoluble residue, which consisted essentially of clays. The leachate solution was decanted off and the residue washed in deionised water, later dried and analysed using the usual procedure.

2) Analysis of the Dolostones

The dolostones were analysed in a similar manner to the limestones. The constituent dolomite was again obtained by leaching, in this instance using nitric acid plus E.D.T.A.. The initial dissolution of the dolostone involved the use of dilute acetic acid (5%) to remove the excess calcite, which commonly occurs in these dolostones as pore-filling cement. Once excess calcite was removed by leaching and the resulting acetate removed by decanting, the remaining dolomite was washed and later leached in dilute nitric acid (5%).

The nitrate was removed and evaporated almost to dryness as calcium nitrate is deliquescent and will not crystallise completely. Therefore, the nitrate was calcined to give CaO, which was then analysed using the procedure outlined at the beginning of Appendix VII. Again, the insoluble residue (mainly clays) was obtained by complete dissolution and analysed in the normal manner.

References

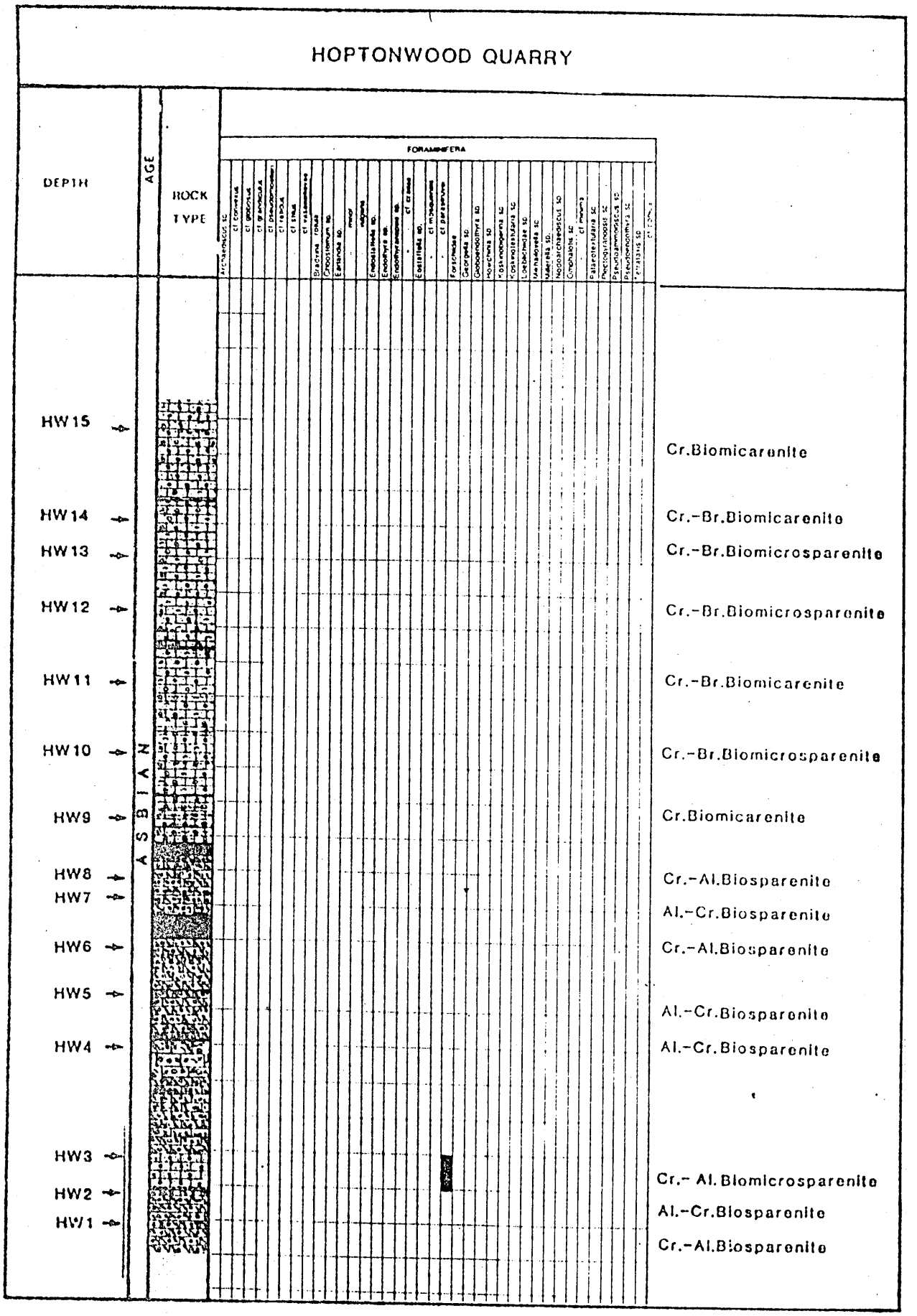
F.J. Flanagan, 1973. "1972 values for international geochemical reference samples" Geochim. et Cosmochim. Acta, V.37, pp. 1189-1200.

F.J. Flanagan, 1976. United States Geological Survey Professional Paper No. 840.

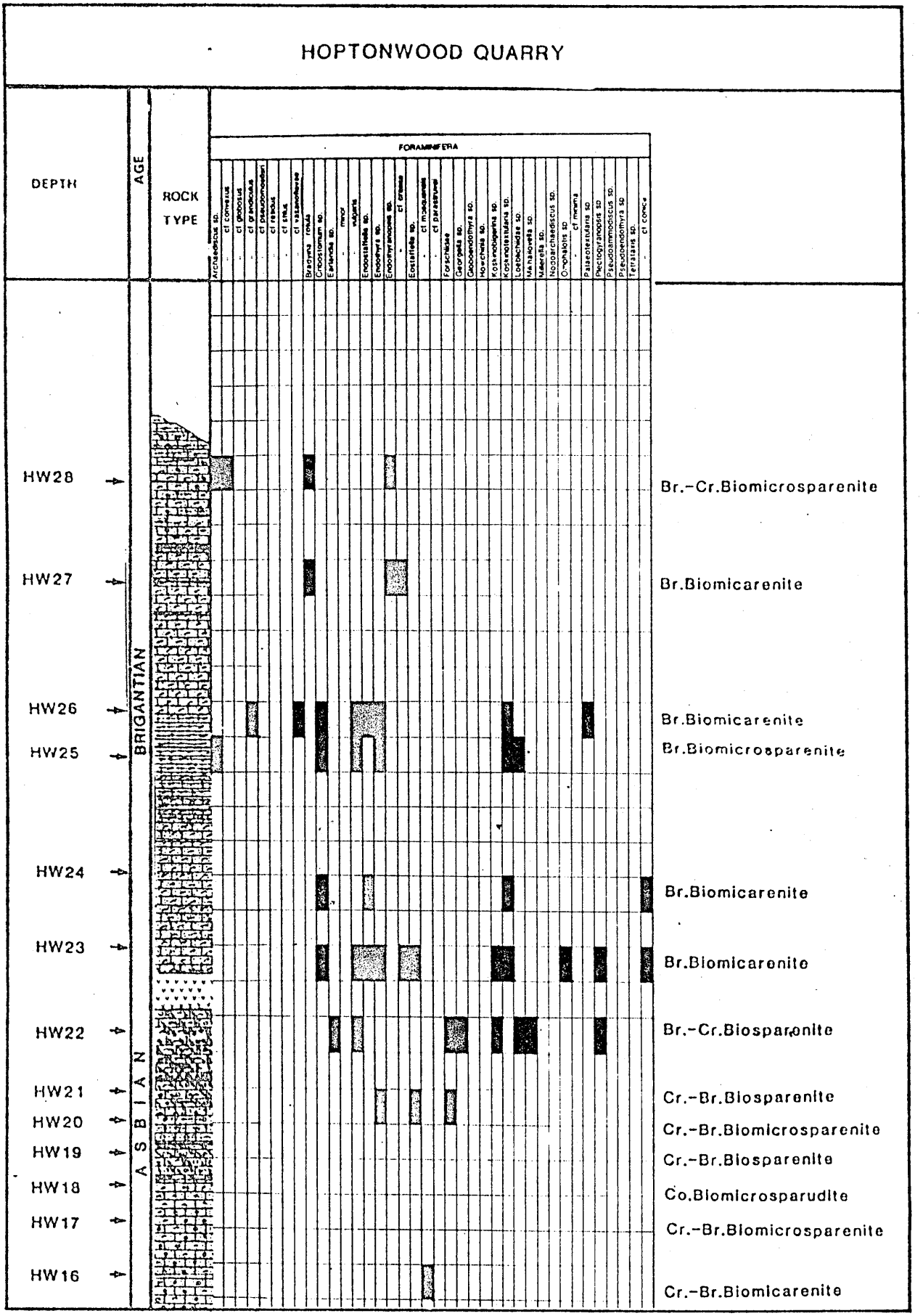
J.T. Routti, 1969. "Sampo, a Fortran IV Program for Computer Analysis of Gamma Spectra from Ge(Li) Detectors, and for other Spectra with Peaks". American Government Report, UCRL - 19452, Oct. 20th 1969, 31p.

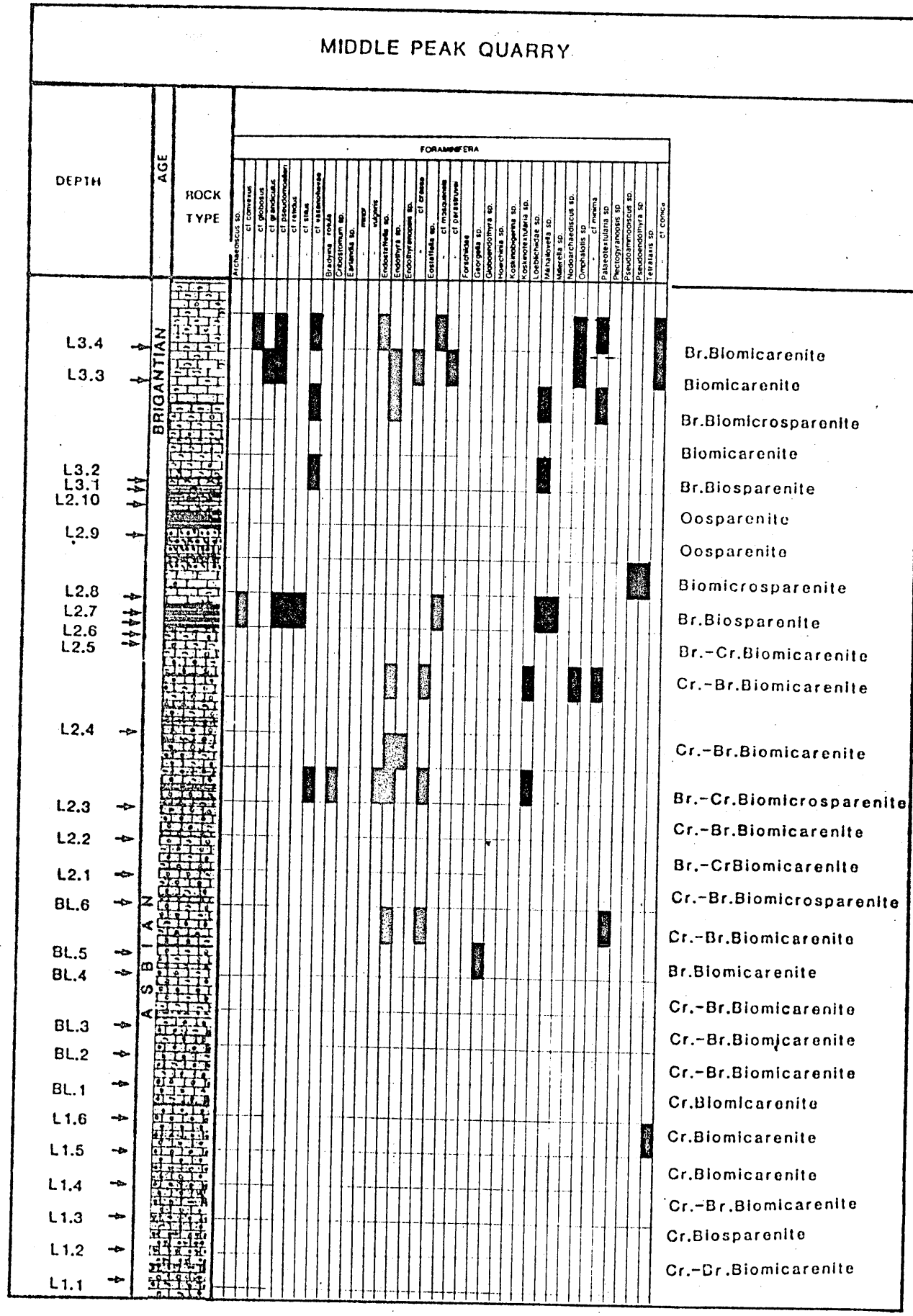
App 11

HOPTONWOOD QUARRY



HOPTONWOOD QUARRY




MIDDLE PEAK QUARRY
DEPTH
AGE
ROCK TYPE
FORAMINIFERA
Archaeoscus sp.
cf. conversus
cf. globosus
cf. grandiculus
cf. pseudomodesti
cf. reticulus
cf. situs
cf. vasseuxhaasa
Bradyina rotula
Cribratomum sp.
Eotuxia sp.
minor
vulgaris
Endostaffella sp.
Endothyra sp.
Endothyranopsis sp.
cf. crassa
Eostaffella sp.
cf. mosquensis
cf. parastruvei
Forschiida
Georgiella sp.
Globoendothyra sp.
Howchinia sp.
Koskinobigenina sp.
Koskinotextularia sp.
Loeblichiidae sp.
Mikhaloviella sp.
Millerella sp.
Nodoarchaediscus sp.
Omphalotis sp.
cf. minima
Palaeotextularia sp.
Plectogyranopsis sp.
Pseudoammoosnus sp.
Pseudoendothyra sp.
Tetrataxis sp.
cf. conica
BRIGANTIAN
ASBIAN
L3.4
L3.3
L3.2
L3.1
L2.10
L2.9
L2.8
L2.7
L2.6
L2.5
L2.4
L2.3
L2.2
L2.1
BL.6
BL.5
BL.4
BL.3
BL.2
BL.1
L1.6
L1.5
L1.4
L1.3
L1.2
L1.1
Br.Biomicarenite
Biomicarenite
Br.Biomicrosparenite
Biomicarenite
Br.Biosparenite
Oosparenite
Oosparenite
Biomicrosparenite
Br.Biosparenite
Br.-Cr.Biomicarenite
Cr.-Br.Biomicarenite
Cr.-Br.Biomicarenite
Br.-Cr.Biomicrosparenite
Cr.-Br.Biomicarenite
Br.-CrBiomicarenite
Cr.-Br.Biomicrosparenite
Cr.-Br.Biomicarenite
Br.Biomicarenite
Cr.-Br.Biomicarenite
Cr.-Br.Biomicarenite
Cr.-Br.Biomicarenite
Cr.Biomicarenite
Cr.Biomicarenite
Cr.Biomicarenite
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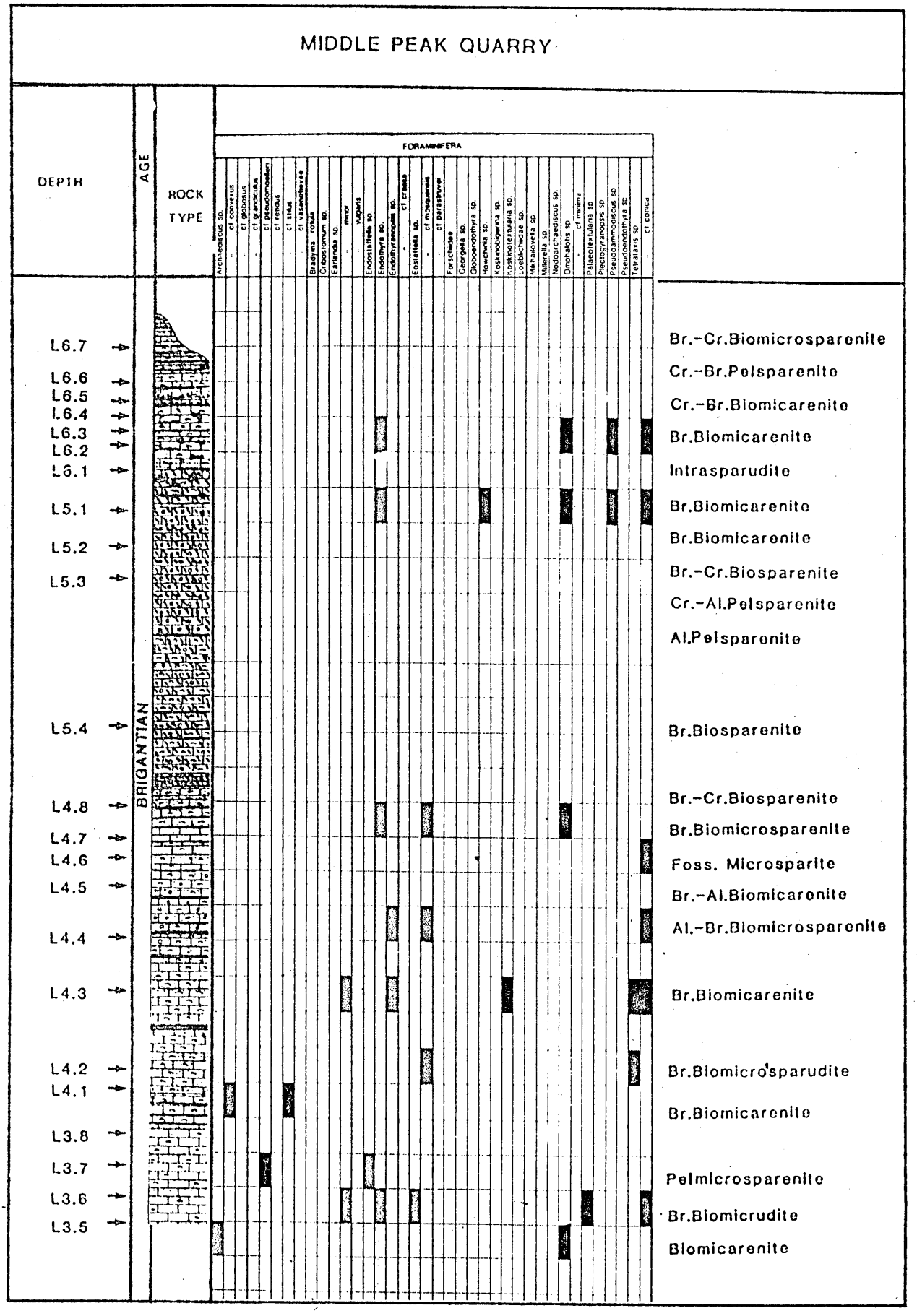
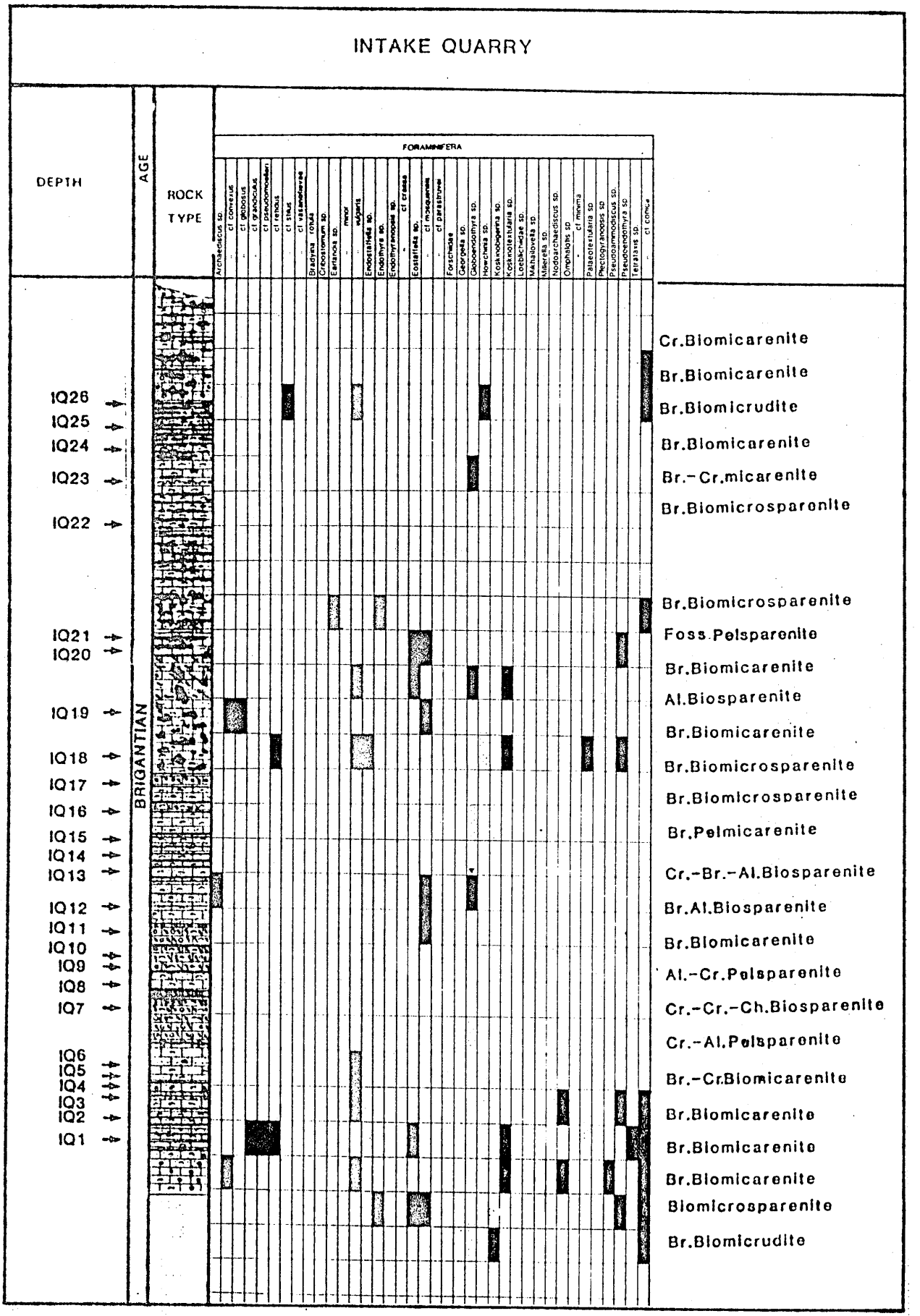
Cr.Biosparenite
Cr.-Br.Biomicarenite


MIDDLE PEAK QUARRY
DEPTH
AGE
ROCK TYPE
FORAMINIFERA
Archaediscus sp.
cf. convexus
cf. gobbosus
cf. grandiculus
cf. pseudomoelleri
cf. rendus
cf. situs
cf. vesiculifera
Bradyina rotula
Cribrostomum sp.
Earlandia sp.
minor
vulgaris
Endostaffella sp.
Endothyra sp.
Endothyranopsis sp.
cf. crassa
Eostaffella sp.
cf. mosquensis
cf. parastruvei
Forschiaia sp.
Georgiella sp.
Globoendothyra sp.
Howchinia sp.
Koskinobigerina sp.
Koskinotextularia sp.
Loeblichiidae sp.
Makhaloyella sp.
Millerella sp.
Nodosarchaediscus sp.
Omphalotis sp.
cf. minima
Palaeotextularia sp.
Plectogyranopsis sp.
Pseudoammodiscus sp.
Pseudoendothyra sp.
Tetrataxis sp.
cf. conica
BRIGANTIAN
L6.7
L6.6
L6.5
L6.4
L6.3
L6.2
L6.1
L5.1
L5.2
L5.3
L5.4
L4.8
L4.7
L4.6
L4.5
L4.4
L4.3
L4.2
L4.1
L3.8
L3.7
L3.6
L3.5
Br.-Cr.Biomicrosparenite
Cr.-Br.Pelsparenite
Cr.-Br.Biomicarenite
Br.Biomicarenite
Intrasparudite
Br.Biomicarenite
Br.Biomicarenite
Br.-Cr.Biosparenite
Cr.-Al.Pelsparenite
Al.Pelsparenite
Br.Biosparenite
Br.-Cr.Biosparenite
Br.Biomicrosparenite
Foss. Microsparite
Br.-Al.Biomicarenite
Al.-Br.Biomicrosparenite
Br.Biomicarenite
Br.Biomicrosparudite
Br.Biomicarenite
Pelmicrosparenite
Br.Biomicrudite
Biomicarenite


INTAKE QUARRY
DEPTH
AGE
ROCK TYPE
FORAMINIFERA
Archaediscus sp.
cf. convexus
cf. globosus
cf. grandiculus
cf. pseudomoelleri
cf. renulis
cf. sinus
cf. vissariensis
Bradyina rotula
Crobostomum sp.
Earlandia sp.
minor
nalpensis
Endostaffella sp.
Endothyra sp.
Endothyranopsis sp.
cf. crassa
Eostaffella sp.
cf. mosquensis
cf. parastruvei
Forschiella
Georgella sp.
Globoendothyra sp.
Howchinia sp.
Koskinobigerina sp.
Koskinotextularia sp.
Loeblichiidae sp.
Mikhaloviella sp.
Millerella sp.
Nodosarchaediscus sp.
Omphalotis sp.
cf. minima
Palaeotextularia sp.
Plectogyranopsis sp.
Pseudoammodiscus sp.
Pseudoendothyra sp.
Tetrataxis sp.
cf. conica
BRIGANTIAN
1Q26
1Q25
1Q24
1Q23
1Q22
1Q21
1Q20
1Q19
1Q18
1Q17
1Q16
1Q15
1Q14
1Q13
1Q12
1Q11
1Q10
1Q9
1Q8
1Q7
1Q6
1Q5
1Q4
1Q3
1Q2
1Q1
Cr.Biomicarenite
Br.Biomicarenite
Br.Biomicrudite
Br.Biomicarenite
Br.-Cr.micarenite
Br.Biomicrosparenite
Br.Biomicrosparenite
Foss.Pelsparenite
Br.Biomicarenite
Al.Biosparenite
Br.Biomicarenite
Br.Biomicrosparenite
Br.Biomicrosparenite
Br.Pelmicarenite
Cr.-Br.-Al.Biosparenite
Br.Al.Biosparenite
Br.Biomicarenite
Al.-Cr.Pelsparenite
Cr.-Cr.-Ch.Biosparenite
Cr.-Al.Pelsparenite
Br.-Cr.Biomicarenite
Br.Biomicarenite
Br.Biomicarenite
Br.Biomicarenite
Biomicrosparenite
Br.Biomicrudite

SAMPLE No.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Zr^{++}	Y^{++}	Sr^{++}	Zn^{++}	Mn^{++}	Ni^{++}	Pb^{++}	Br^{-}	L.O.I.	Total
1A	1.26	0.28	0.09	0.24	52.76	4.8	7.4	359	8.9	533	8.3	14.3	10.8	43.13	97.85
1B	1.23	0.29	1.13	3.93	48.96	4.3	7.7	165	22.6	2574	0.0	26.2	10.4	43.59	99.41
1C	1.04	0.00	2.86	16.71	33.90	3.3	4.5	51	34.2	4796	0.0	35.3	15.3	45.79	100.79
1D	1.96	0.14	0.33	20.53	30.64	6.1	5.9	62	42.9	880	9.9	35.5	19.0	46.56	100.27
2A	1.56	0.68	0.08	0.30	52.31	4.5	7.8	389	16.8	497	0.0	8.6	10.4	43.22	98.24
2B	3.61	0.12	2.29	11.35	39.84	4.5	7.4	94	31.1	5645	6.4	31.7	11.6	42.94	100.46
2C	2.06	0.14	1.17	19.60	32.53	5.8	5.6	69	66.4	2264	2.1	50.9	16.4	44.69	100.44
3A	0.24	0.10	0.02	0.17	54.27	3.3	4.1	246	0.0	129	7.7	6.4	9.8	42.51	97.35
3B	0.17	0.10	0.02	0.14	53.82	0.0	2.7	198	0.0	189	0.0	5.9	9.7	43.67	97.96
3C	0.49	0.00	0.57	20.29	30.39	3.5	4.4	48	109.0	1157	0.0	8.7	19.4	47.96	99.84
4A	0.27	0.09	0.02	0.23	53.63	0.0	1.5	170	13.0	156	3.6	31.8	9.8	43.58	97.86
4B	0.24	0.09	0.03	0.23	53.47	0.0	1.9	170	12.6	123	3.3	13.7	9.9	43.61	97.70
4C	0.18	0.00	0.41	21.05	31.41	3.7	4.3	55	15.1	1378	4.0	8.9	15.4	46.50	99.70
5A	----	----	----	-----	-----	2.4	3.2	389	21.6	161	4.2	36.2	10.7	-----	-----
5B	----	----	----	-----	-----	3.6	4.7	33	159.2	636	6.4	9.6	15.3	-----	-----
6A	1.01	0.05	0.26	19.22	34.88	2.6	3.7	91	14.0	1049	0.0	13.2	10.4	43.36	98.90
6B	0.09	0.00	0.56	5.38	48.17	2.3	3.7	92	190.1	1610	4.5	98.2	10.4	44.65	99.05
6C	2.10	0.09	0.14	0.14	52.62	3.0	10.7	92	196.5	797	3.7	525.5	10.3	43.08	98.33
6D	0.12	0.02	1.07	1.21	52.18	2.0	5.2	103	373.8	2961	9.3	48.7	9.5	43.58	98.53
6E	0.27	0.20	1.02	2.18	47.84	4.1	1.0	119	527.0	2005	0.0	611.1	9.5	39.71	91.55
6F	0.13	0.05	0.54	0.45	52.62	3.3	0.0	431	840.8	2464	1.7	987.0	11.3	43.71	97.97
7A	0.25	0.06	0.09	0.13	55.78	2.8	2.5	106	185.8	775	9.6	59.0	10.1	41.92	98.35
7B	0.42	0.04	0.29	0.12	53.58	3.2	5.7	73	733.6	2784	18.6	205.0	9.9	43.57	98.40
7C	0.03	0.00	0.42	20.60	31.92	3.4	4.3	28	508.7	1491	10.4	37.6	17.5	47.19	100.37
7D	0.06	0.00	0.62	11.56	42.32	3.5	4.3	45	757.6	2483	17.6	215.0	11.5	45.89	100.80
8A	0.52	0.29	0.07	0.13	53.33	3.7	9.1	208	23.9	184	0.0	9.2	9.9	43.34	97.72
8B	0.03	0.02	0.06	0.06	53.72	2.1	3.5	125	61.5	670	8.6	12.5	10.0	43.78	97.76
8C	0.07	0.00	0.35	21.90	30.49	3.1	3.0	38	19.4	1302	5.9	7.3	15.6	47.22	100.17
8D	0.34	0.00	0.12	0.02	53 91	2.2	4.7	126	88.1	1409	3.7	5.5	10.3	43.70	98.26
8E	0.25	0.00	0.31	0.10	54.52	0.0	7.6	100	163.6	2260	2.5	12.2	10.3	40.63	96.07
8F	0.48	0.00	0.21	0.03	53.89	2.2	5.1	107	169.6	1943	0.0	9.8	10.9	43.08	97.91
8G	0.14	0.00	0.64	6.01	48.05	2.3	5.9	67	998.0	2200	20.9	103.1	11.1	43.88	99.06
8H	0.02	0.00	0.26	21.35	30.36	2.9	6.0	54	666.5	1357	6.5	123.7	17.0	47.72	99.93
8I	0.06	0.00	0.23	16.69	37.18	2.5	3.8	35	283.3	1124	5.8	33.3	17.6	46.71	101.02

SAMPLE No.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Zr^{++}	Y^{++}	Sr^{++}	Zn^{++}	Mn^{++}	Ni^{++}	Pb^{++}	Br^{-}	L.O.I.	Total
9A	0.07	0.00	0.53	20.67	31.50	3.6	4.0	25	33.5	1530	3.5	10.5	20.0	47.32	100.25
9B	0.03	0.00	0.43	21.30	30.82	3.2	3.7	25	48.8	1381	4.4	13.3	21.4	47.50	100.23
9C	0.70	0.15	0.07	0.30	54.07	3.6	4.8	170	22.6	576	1.5	273.5	10.3	43.21	98.61
10A	0.08	0.00	0.43	22.73	33.68	0.0	3.0	29	45.1	1696	0.0	31.8	20.1	43.29	100.39
10B	0.02	0.00	0.37	23.61	33.19	0.0	6.9	92	366.0	1838	11.4	165.6	10.5	43.70	101.14
10C	0.25	0.05	0.41	0.10	52.84	0.0	6.0	100	242.0	1929	3.0	9.5	11.1	43.79	97.89
10D	0.15	0.02	0.00	0.14	53.16	0.0	4.7	100	46.7	1295	2.6	6.8	10.8	43.82	97.44
10E	0.26	0.11	0.75	0.07	52.28	0.0	6.1	109	347.4	1526	2.6	9.5	11.2	43.59	97.26
10F	0.25	0.00	0.16	0.08	52.95	0.0	5.1	117	16.3	724	10.7	6.0	10.6	43.93	97.46
Limestone Samples:															
HW1	0.03	0.04	0.02	0.01	53.94	0.0	7.6	140	13.5	94	2.7	86.5	10.3	42.91	97.26
HW8	0.25	0.09	0.03	0.11	53.55	0.0	7.6	160	11.8	124	1.0	13.4	10.4	43.33	97.39
HW18	0.56	0.06	0.04	0.12	53.27	0.0	6.2	398	1.2	119	11.3	40.6	11.3	43.95	98.06
HW26	0.87	0.16	0.09	0.27	51.96	0.0	2.6	369	36.9	536	0.0	114.1	10.3	43.99	97.45
IQ7	0.76	0.06	0.07	0.16	53.53	0.0	4.4	243	14.2	559	1.2	11.1	10.6	43.57	98.23
IQ16	1.60	0.31	0.04	0.26	53.04	0.0	6.3	404	9.0	122	0.0	42.2	11.3	43.29	98.60
IQ20	0.72	0.17	0.05	0.29	53.06	0.0	5.1	414	1.9	164	8.1	11.2	10.9	43.52	97.87
$L_1 6$	1.65	0.02	0.02	0.59	53.01	0.0	1.9	252	18.9	130	5.9	12.1	11.0	42.99	98.32
$L_2 7$	2.06	1.76	0.14	0.40	51.21	9.4	11.5	444	44.5	241	1.5	17.2	11.2	42.83	98.48
$L_2 10$	0.30	0.02	0.04	0.24	52.98	0.0	5.4	329	37.8	239	0.0	48.3	10.7	43.88	97.53
$L_4 5$	1.78	0.09	0.11	0.14	52.85	0.0	5.1	336	29.3	355	8.2	8.5	10.5	43.08	98.13
$L_6 2$	2.16	0.44	0.05	0.33	52.60	2.9	7.8	485	17.1	155	6.6	85.9	11.1	42.84	98.50
$L_6 6$	1.06	0.32	0.03	0.15	53.07	5.5	10.1	478	20.0	207	9.7	72.0	11.0	43.36	98.07

Oxides in % Elemental concentrations in p.p.m.

SAMPLE No.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Zr^{++}	Y^{++}	Sr^{++}	Zn^{++}	Mn^{++}	Ni^{++}	Pb^{++}	Br^{-}	L.O.I.	Total
3-6m	0.70	0.03	0.97	13.71	39.01	2.9	6.8	33	121.1	1109	11.7	12.1	16.8	46.40	100.95
6-9m	1.67	0.00	0.51	19.92	31.29	2.8	5.8	58	80.5	1063	1.6	29.2	24.7	46.82	100.33
9-12m	0.25	0.00	0.49	21.01	29.73	2.9	5.8	33	65.0	1178	6.8	111.7	26.4	48.60	100.22
12-15m	1.18	0.07	1.01	20.65	29.66	4.1	12.8	64	126.3	2033	3.0	452.7	15.0	47.39	100.23
15-18m	0.41	0.00	0.67	20.12	32.06	4.4	8.8	37	158.4	1442	8.0	180.5	15.1	47.14	100.27
18-21m	0.05	0.00	0.83	21.29	31.10	3.1	5.9	47	107.4	1231	7.2	154.1	20.1	47.01	100.44
21-24m	0.95	0.48	0.63	21.60	29.93	7.4	7.7	54	59.3	1068	3.0	126.0	20.2	46.76	100.48
24-27m	0.14	0.00	0.48	21.60	30.47	3.0	8.8	61	75.5	1172	4.9	111.6	21.8	47.65	100.48
27-30m	0.02	0.00	0.35	19.30	32.45	0.0	6.0	51	114.6	989	3.3	21.7	21.1	47.33	99.57
30-33m	0.05	0.00	0.30	19.92	32.07	2.9	6.2	69	83.9	861	5.0	19.3	20.4	47.51	99.95
33-36m	0.02	0.00	0.32	21.44	31.40	2.8	6.1	55	73.9	876	8.2	35.9	23.7	47.68	101.09
36-39m	0.00	0.00	0.32	21.54	30.20	2.9	6.4	51	65.8	854	1.1	62.1	24.0	47.89	100.02
39-42m	0.00	0.00	0.40	21.54	30.62	3.1	4.7	63	87.5	946	0.0	18.0	25.5	47.83	100.50
42-45m	0.13	0.00	0.35	20.19	29.91	4.4	5.4	63	77.0	925	0.0	26.1	25.7	47.97	98.67
45-48m	0.03	0.00	0.34	21.54	30.55	2.8	4.1	58	40.2	1018	0.0	54.6	24.0	47.88	100.46
48-51m	0.09	0.00	0.26	20.34	31.58	3.1	3.8	55	48.3	953	0.0	32.2	23.1	47.69	100.07
51-54m	0.11	0.00	0.26	20.75	31.05	0.0	3.8	73	52.9	1015	0.0	54.6	24.0	47.59	99.88
55-58m	0.11	0.00	0.27	20.41	31.96	2.7	5.1	61	38.3	865	0.0	39.0	23.8	47.80	99.85
58-61m	0.19	0.00	0.26	20.77	30.39	3.1	6.3	61	15.3	926	3.0	28.0	24.7	47.73	99.45
61-64m	0.00	0.00	0.27	20.93	30.87	0.0	5.2	71	38.2	855	0.0	13.6	19.6	47.77	99.94
64-67m	0.03	0.00	0.19	20.93	30.27	2.6	3.4	60	16.2	603	0.0	7.1	30.5	48.56	100.05
67-70m	0.00	0.00	0.33	20.88	30.90	3.1	5.4	80	49.8	1009	0.0	6.0	22.1	47.70	99.93
70-73m	0.00	0.00	0.29	20.60	30.16	0.0	6.2	69	35.9	873	0.0	6.0	23.4	49.10	100.25
73-76m	0.00	0.00	0.22	20.51	28.91	0.0	4.2	99	5.6	819	2.8	7.4	27.6	49.76	99.47
76-79m	0.00	0.00	0.47	20.93	31.05	2.4	7.0	54	43.7	1012	0.0	61.0	21.9	47.57	100.14
79-82m	0.05	0.00	0.23	20.73	31.34	2.5	3.6	53	1.5	632	0.0	5.7	25.0	47.86	100.28
82-85m	----	----	----	-----	-----	0.0	6.4	66	17.5	764	0.0	12.5	21.9	-----	------
85-88m	0.10	0.00	0.35	21.12	30.60	3.5	5.2	52	16.9	849	0.0	12.1	18.2	47.66	99.93
88-91m	0.01	0.00	0.28	21.35	31.11	3.5	4.5	47	21.7	713	4.9	98.0	20.2	47.85	100.69
91-94m	0.00	0.00	0.31	21.06	30.72	0.0	4.5	81	36.0	964	0.0	24.0	25.5	47.79	99.99
94-97m	0.17	0.00	0.30	20.98	30.18	4.2	5.9	65	23.3	826	9.4	36.1	23.0	47.90	99.63
97-100m	0.71	0.37	0.35	19.75	29.13	9.8	8.6	56	22.2	836	6.3	21.8	21.4	48.84	99.25
100-103m	0.52	0.23	0.28	20.81	31.12	9.1	5.0	47	4.4	667	0.0	38.3	20.7	47.34	100.38
103-106m	0.05	0.00	0.28	21.49	31.73	0.0	5.5	51	31.8	603	2.1	9.3	20.1	47.62	101.24

SAMPLE No.	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Zr^{++}	Y^{++}	Sr^{++}	Zn^{++}	Mn^{++}	Ni^{++}	Pb^{++}	Br^{-}	L.O.I.	Total
106-109m	0.06	0.00	0.34	21.52	31.10	3.0	4.5	61	5.6	748	0.0	9.8	22.1	47.68	100.79
109-112m	0.34	0.06	0.34	20.98	30.99	5.9	4.1	63	8.0	760	1.2	25.7	20.4	47.23	100.03
112-115m	----	----	----	-----	-----	3.9	3.7	44	26.9	732	0.0	20.8	20.1	-----	------
115-118m	0.07	0.00	0.17	19.45	30.06	2.7	2.7	45	54.6	1053	1.6	9.1	21.6	47.55	97.42
118-121m	0.00	0.00	0.33	18.08	34.53	2.5	4.2	63	50.3	1125	4.1	12.0	18.2	47.17	100.24
121-124m	0.00	0.00	0.35	19.25	33.47	2.4	6.8	77	40.8	1039	0.0	14.5	20.7	47.54	100.73
124-127m	0.00	0.00	0.23	20.22	32.31	3.0	4.5	72	18.2	804	0.0	18.6	28.3	47.55	100.40
127-130m	0.00	0.00	0.27	20.89	30.92	2.5	4.7	86	18.9	930	1.4	11.9	28.0	47.83	100.02
130-133m	0.00	0.00	0.28	21.28	30.80	4.4	5.3	57	16.7	1096	0.0	20.9	24.6	47.90	100.38
133-136m	0.00	0.00	0.31	20.90	31.48	---	---	48	----	----	---	----	----	47.62	------
136-139m	0.00	0.00	0.30	21.46	30.71	---	---	--	----	----	---	----	----	47.57	------
139-142m	0.00	0.00	0.28	20.36	31.26	3.5	7.3	52	21.5	837	8.4	10.1	21.1	47.76	99.76
142-145m	0.00	0.00	0.26	21.05	30.39	3.2	4.0	92	9.9	927	0.0	6.3	24.9	48.54	100.35
145-148m	0.00	0.00	0.24	20.97	31.52	3.2	3.6	79	20.0	954	0.0	6.2	24.4	47.80	100.64
148-151m	0.02	0.00	0.37	20.89	30.90	0.0	5.1	88	131.6	1575	0.0	23.9	24.6	47.86	100.24
151-154m	0.09	0.00	0.32	21.33	30.61	4.3	5.2	76	80.6	1342	3.8	33.9	26.4	47.77	100.28
154-157m	0.06	0.00	0.32	21.16	30.64	3.7	5.4	81	87.3	50	3.2	28.5	27.1	47.68	99.89
157-160m	0.05	0.00	0.33	21.23	30.63	3.2	4.2	58	48.4	1121	0.0	12.4	22.5	47.68	100.05
160-163m	0.05	0.00	0.33	21.16	31.13	2.4	5.6	77	63.2	1016	0.0	13.4	21.1	47.96	100.75
163-166m	0.00	0.00	0.33	18.29	34.87	4.8	7.4	77	198.2	1472	2.7	74.1	23.3	47.26	100.94
166-169m	1.05	0.00	0.45	21.11	30.73	5.1	6.5	67	208.5	1245	3.6	74.0	21.1	46.93	100.43
169-172m	14.71	0.27	0.76	16.91	23.38	6.8	42.5	123	254.3	1058	4.9	94.6	18.3	36.76	92.95
New Harborough Farm Borehole.															
B_2P_5	0.33	0.00	0.30	16.21	36.73	0.0	5.0	87	379.3	990	2.0	337.5	32.6	46.91	100.46
B_2P_7	0.02	0.00	0.33	20.02	34.07	0.0	11.8	53	231.6	1106	2.8	4.5	31.1	47.55	102.13
B_2P_{11}	0.19	0.00	0.42	21.42	35.35	0.0	6.8	65	251.0	1485	7.7	3.5	19.2	43.64	101.20
B_2P_{13A}	0.00	0.00	0.47	19.44	32.84	0.0	6.3	86	301.0	1813	1.4	4.9	19.6	47.73	100.70
B_2P_{14}	0.07	0.00	0.52	19.64	32.99	0.0	7.7	70	281.7	1744	2.5	5.1	19.1	47.64	101.07
B_2P_{15}	0.41	0.00	0.56	20.03	30.18	0.0	9.4	53	277.9	1282	13.3	7.9	23.7	47.48	98.83
B_2P_{17}	0.02	0.00	0.33	19.73	33.99	0.0	6.0	63	93.6	1135	5.0	3.8	25.1	47.55	101.75
B_2P_{25}	3.70	0.12	0.56	20.01	30.18	5.2	8.7	66	45.8	1073	13.5	102.2	15.4	45.58	100.32

Oxides in % Elemental concentrations in p.p.m.

Limestone-Correlation Coefficients. Sample size = 38

	ZR	Y	SR	ZN	MN	NI	PB	BR	SI	AL	FE	MG
Y	0.45											
SR	0.18	0.23										
ZN	-0.34	0.03	0.12									
MN	0.17	-0.03	0.23	0.06								
NI	0.28	0.35	0.09	0.56	0.03							
PB	0.08	0.07	0.43	0.06	0.04	0.46						
BR	0.14	0.04	0.02	0.08	0.13	0.04	0.03					
SI	0.34	0.51	0.75	0.64	0.07	0.01	0.12	0.03				
AL	0.12	0.14	0.33	-0.03	0.27	0.32	0.04	0.23	0.21			
FE	0.32	0.22	0.87	0.24	0.80	0.07	0.31	0.13	0.04	0.99		
MG	0.09	0.25	0.24	0.09	0.05	0.23	0.04	0.09	0.21	0.23	0.09	
CA	0.19	0.17	0.16	0.13	0.13	0.03	0.02	0.13	-0.09	0.09	0.34	0.34

Dolostone-Correlation Coefficients. Sample Size = 80

	ZR	Y	SR	ZN	MN	NI	PB	BR	SI	AL	FE	MG	CA
Y	0.32												
SR	0.07	0.32											
ZN	0.09	0.16	-0.13										
MN	0.04	0.06	-0.03	0.06									
NI	0.22	0.06	-0.13	0.69	-0.13								
PB	0.04	0.18	-0.02	0.29	0.14	0.04							
BR	-0.11	0.04	0.02	-0.42	-0.19	-0.47	-0.18						
SI	0.32	0.90	0.30	0.05	0.13	0.04	0.09	0.11					
AL	****	****	****	****	****	****	****	****	0.43				
FE	0.12	0.13	0.05	0.11	0.80	0.07	0.25	0.36	0.28	0.18			
MG	0.20	0.09	-0.63	-0.13	0.27	0.58	0.20	0.82	0.05	-0.27	-0.19		
CA	****	****	****	****	****	****	****	****	0.15	****	0.12	0.89	
CaO_{MgO}	0.17	-0.02	0.12	-0.03	-0.03	-0.04	-0.05	-0.32	0.02	-0.04	****	0.43	****

Rare Earth Element Concentrations.

	SAMPLE NO.	La	Ce	Nd	Sm	Eu	Gd	Tb	Tm	Yb	Lu
	MD1(lst.)	1.66	1.24	0.92	0.36	0.05	0.00	0.04	0.00	0.12	0.00
L_16	MD2(calc.$^-$)	2.09	1.65	0.00	0.35	0.06	0.00	0.05	0.00	0.16	0.00
	MD3(calc.$^+$)	2.12	1.81	0.00	0.16	0.07	0.00	0.06	0.00	0.20	0.00
G.G.	MD6(dst.)	1.40	1.50	1.10	0.40	0.11	0.30	0.05	0.03	0.19	0.00
	MD7A(p.calc.$^-$)	1.15	0.87	0.47	0.21	0.05	0.00	0.03	0.05	0.09	0.02
G.G.	MD7B(dol.$^-$)	1.04	0.93	0.62	0.22	0.04	0.00	0.04	0.02	0.11	0.11
	MD8(dol.$^-$)	1.41	1.20	0.89	0.26	0.11	0.00	0.04	0.00	0.15	0.01
	MD9(g.lst.)	4.70	7.60	4.70	1.20	0.26	0.90	0.14	0.10	0.39	0.04
	MD10(g.calc.$^+$)	4.58	6.96	5.22	1.11	0.25	0.95	0.14	0.11	0.36	0.05
	MD11(dol.$^-$)	2.10	3.19	2.75	0.63	0.14	0.46	0.11	0.05	0.34	0.06
Mn.Q	MD12(lst.)	1.81	1.70	1.24	0.51	0.09	0.52	0.07	0.04	0.17	0.04
	MD13(calc.$^+$)	1.90	1.37	1.06	0.51	0.08	0.36	0.06	0.05	0.17	0.00
Mn.Q	MD15(lst.)	2.20	3.30	0.00	0.10	0.00	0.00	0.10	0.00	0.37	0.04
	MD16(calc.$^+$)	2.63	5.66	5.33	1.26	0.27	1.14	0.21	0.06	0.40	0.05
	MD17(dol.)	1.23	1.46	1.02	0.43	0.06	0.23	0.04	0.02	0.11	0.00
H.R.	MD18(dst.)	1.60	1.45	1.08	0.33	0.06	0.30	0.04	0.03	0.13	0.02
	MD19(p.calc.$^+$)	2.62	2.48	0.00	0.55	0.11	0.00	0.11	0.00	0.16	0.00
	MD21(dst.)	1.10	0.90	0.60	0.20	0.05	0.00	0.03	0.02	0.14	0.02
G.G.	MD22(p.calc.$^+$)	1.41	0.40	0.00	0.17	0.49	0.00	0.00	0.00	1.04	0.00
	MD24(clay)	1.96	20.66	10.24	0.11	0.25	0.00	0.41	0.53	1.12	0.05

lst. = complete limestone. dst. = complete dolostone.

calc. = calcite obtained from dissolution experiments.

p.calc. = pore-filling calcite.

dol. = dolomite obtained from dissolution experiments.

g.lst. = gangue limestone.

g.calc. = gangue calcite obtained from dissolution experiments.

$^+$dissolution using E.D.T.A.

$^-$dissolution not using E.D.T.A.

Rare Earth Element Concentrations

	SAMPLE NO.	La	Ce	Nd	Sm	Eu	Gd	Tb	Tm	Yb	Lu
	MD25(lst.)	1.47	1.25	1.70	0.64	0.10	0.41	0.08	0.04	0.20	0.23
HW26	MD26(calc.$^{+}$)	2.23	1.25	1.17	0.57	0.13	0.40	0.09	0.41	0.27	0.03
	MD27(clay)	12.15	16.76	12.35	2.99	0.41	0.19	0.28	0.65	0.80	0.12
	MD29(dst.)	1.30	0.90	0.00	0.50	0.05	0.20	0.04	0.02	0.12	0.02
	MD30(p.calc.$^{-}$)	1.30	0.28	0.00	0.27	0.52	0.00	0.00	0.51	0.25	0.00
G.G.	MD32(dst.)	0.99	0.81	0.62	0.21	0.04	0.00	0.03	0.03	0.11	0.02
	MD33(dst.)	1.10	0.70	0.60	0.20	0.04	0.20	0.03	0.02	0.13	0.02
	MD34(dst.)	1.49	0.60	0.33	0.29	0.01	0.00	0.01	0.00	0.02	0.00
$L_1$6	MD35(clay^{-})	4.25	60.59	35.85	0.78	0.85	0.00	0.55	0.32	1.37	0.00
	MD37(clay^{-})	10.22	21.13	3.63	1.69	0.21	0.00	0.19	0.14	0.87	1.19
G.G.	MD38(clay^{+})	3.39	3.60	2.71	0.57	0.03	0.00	0.00	0.08	0.42	0.00
	MD39(clay^{-})	8.40	16.40	4.95	1.33	0.12	0.00	0.07	0.07	0.41	0.00
	MD28(p.calc.$^{-}$)	2.21	1.58	0.95	0.32	0.08	0.47	0.05	0.05	0.32	0.03
121-124	MD40(dol.$^{-}$)	1.33	1.66	1.02	0.35	0.05	0.31	0.05	0.04	0.22	0.29
HW26	MD41(calc.$^{-}$)	2.21	0.95	2.06	0.47	0.14	0.73	0.09	0.06	0.27	0.03
	MD42(clay^{-})	9.90	15.20	7.60	1.90	0.35	0.00	0.23	0.33	0.86	0.12
3-6	MD43(dst.)	1.40	1.30	1.30	0.30	0.07	0.50	0.09	0.06	0.25	0.04
36-39	MD44(dst.)	2.00	1.60	1.60	0.40	0.10	0.50	0.07	0.06	0.31	0.05
70-73	MD45(dst.)	2.30	1.90	1.70	0.60	0.08	0.30	0.07	0.05	0.28	0.05
103-106	MD46(dst.)	2.00	2.00	1.60	0.50	0.06	0.40	0.06	0.06	0.27	0.05
136-139	MD47(dst.)	1.90	1.50	1.50	0.40	0.07	0.60	0.07	0.05	0.26	0.04
133-136	MD48(p.calc.$^{-}$)	2.53	1.58	1.90	0.32	0.08	0.00	0.06	0.03	0.25	0.03
	MD49(dol.)	1.82	1.30	1.31	0.34	0.06	0.41	0.05	0.04	0.22	0.29
	MD50(min.)	2.89	4.42	3.73	1.10	0.23	1.12	0.16	0.08	0.41	0.54

lst. = complete limestone. dst. = complete dolostone. min. = mineralisation

calc. = calcite obtained from dissolution experiments. $^{+}$dissolution using E.D.T.A.

p.calc. = pore-filling calcite obtained from dissolution experiments. $^{-}$dissolution not using E.D.T.A.